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(54) Title: CATALYST COMPOSITIONS AND PROCESSES FOR OLEFIN POLYMERS AND COPOLYMERS

(57) Abstract

The present invention is directed to certain novel late transition metal salicylaldimine chelates and, further, to novel bidentate ligand compounds of substituted salicylaldimine, and their utility as polymerization catalysts alone or in combination with adjunct agent and/or Lewis base in processes of polymerizing olefin monomers and copolymerizing olefin monomers with functionalized olefin monomers.

CATALYST COMPOSITIONS AND PROCESSES
FOR OLEFIN POLYMERS AND COPOLYMERS

This application is a continuation-in-part
application of copending U.S. application Serial No.
08/822,531, filed March 24, 1997 which is incorporated
herein in its entirety by reference.

This invention was made with United States
Government support under Contract No. 70NANB5H1136
awarded by the Department of Commerce's National
Institute of Standards and Technology. The United States
has certain rights in the invention.

The present invention is directed to organometallic
catalysts and catalyst compositions useful in the
polymerization of alpha-olefins alone or in combination
with functionalized olefins, certain bidentate ligand
compounds useful in providing the subject catalysts,
processes of forming the bidentate ligand compounds and
catalysts therefrom, processes of forming olefin
oligomers and polymers utilizing the subject catalysts
and catalyst compositions, and the oligomers and polymers
formed therefrom.

The polyolefin industry has relied on various
catalyst and initiator systems. The polymerization of
ethylene and other non-polar 1-olefins has been commonly
accomplished using organometallic Ziegler-Natta
coordination-type catalysts, chromium catalysts, other
early transition metal catalysts, as well as free-radical
type initiators. Although the array of catalysts
available provides different approaches to the
manufacture of polyolefins with differing physical and
mechanical properties, these catalysts are highly
susceptible to a range of substances which poison or
deactivate the catalyst's activity. It is well known
that even trace amounts of oxygen, carbon monoxide,

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acetylene or water causes deactivation. Further,
catalyst deactivation is caused by organic compounds
having oxygen donor groups such as ethers, esters,
alcohols, or ketones. Industrial application of these
organometallic catalysts requires careful and elaborate
measures to assure the absence of such poisons. Because
these catalysts are easily poisoned, they tend to form
low molecular weight materials, can not be used to
provide copolymerization of ethylene with an oxygenated
functional monomer, such as an ester, acid or ether
functionalized olefin, and generally may produce highly
branched polymer products.

More recently, olefin polymerizaton catalysts have
been developed which are less oxophilic than the early
transition metal counterparts. For example, U.S. Patents
4,310,716; 4,382,153; 4,293,727; 4,301,318; and 4,293,502
each disclose late transition metal (e.g. Ni) complexes
which provide low molecular weight oligomers of ethylene.
Further, polymerization of ethylene has been successfully
shown using complexes based on phosphorous ylide ligands
in U.S. Patent 4,537,982 as well as in U.S. Patents
4,698,403; 4,716,205; and 4,906,754. These nickel based
catalysts formed from P-O bidentate ligands have been
shown to provide high activity in the oligomerization and
polymerization of ethylene. Still more recently, L. K.
Johnson et al in J. Am. Chem. Soc. 1995 117, 6414,
reported the formation and use of Pd(II) and Ni(II) based
cationic complexes formed from diimine ligands to provide
high molecular weight polyolefins. Finally, WO 96/23010
describes a process for the polymerization of olefins
using a variety of transition metal complexes of certain
diimine bidentate ligands. In many cases the
polymerizations provided highly branched polyolefins and
were not shown to be useful in providing functionalized

copolymer products. Further, in those instances where functionalized copolymers were formed, it was shown that the functional groups reside exclusively at the end of chain branches.

Certain processes and cationic nickel (II) catalyst compositions have been described also by L.K. Johnson et al in WO 97/02298. These cationic complexes are described as active for the polymerization of ethylene and other olefins. They require use of an acid of a non-coordinating mono-anion, or some combination of compounds that will generate such acid, in order for the catalyst composition to be rendered active towards olefin polymerization. The present neutral complexes, as well as the use of a Lewis base is not suggested by Johnson et al.

Although Löfgren et al, in Macromolecules 1997, 30, 171-175 describe polymerization of ethylene by cationic zirconium salen bis-chloride complexes with or without a Lewis base (tetrahydrofuran), they show that the catalyst composition exhibits only low levels of activity. There are many references to the deleterious effect of Lewis base toward late transition metal catalyst compositions as well as single-site catalyst compositions of the metallocene type. For example, EP 94/304642 and EP 94/630910 disclose that Lewis base, such as dialkyl ether, substantially terminates olefin polymerization by a single-site catalyst composition composed of a metallocene compound and partially hydrolyzed aluminum alkyl compound (aluminoxane). Additionally, U.S. 5,571,881 and WO 95/14048 indicate that an unsaturated Lewis base, e.g., vinyl ether, either reacts with the cationic late transition metal catalysts to destroy their activity or causes reduction of the resultant polymer molecular weight.

It is highly desired to provide a catalyst for the oligomerization and polymerization of olefins, in particular ethylene, which provides a substantially linear (low degree of branching) product. It is also highly desired to provide a nonionic catalyst which can provide the linear polymer product. It is still further desired to provide a nonionic catalyst which is capable of providing a product of high molecular weight which is substantially linear and, optionally, which is capable of promoting copolymerization of olefin and functionalized olefin monomer units.

Finally, it is desired to provide a catalyst composition composed of a non-ionic catalyst in combination with an adjunct agent and/or a Lewis base which is capable of providing a product of high molecular weight which is substantially linear and, optionally, which is capable of promoting copolymerization of olefin and functionalized olefin monomer units.

Summary of the Invention

The present invention is directed to certain late transition metal salicylaldimine chelates as olefin polymerization catalysts, to bidentate ligand compounds of substituted salicylaldimine which are precursors for said catalysts, to catalyst compositions composed of said salicylaldimine chelates in combination with an adjunct agent and/or a Lewis base, the methods of forming said precursor compounds and said catalysts, and the method of polymerizing olefin monomers, especially ethylene, as well as copolymerization of olefin and functionalized olefin monomers. Each of the above elements of the present invention is fully described herein below.

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Detailed Description

The present invention provides a process for polymerizing olefin monomers, in particular ethylene, in the presence of catalysts taken from the selected family of salicylaldimine late transition metal chelates and to catalyst compositions composed of said salicylaldimine chelates in combination with an adjunct agent and/or a Lewis base, to produce polyolefins which can be substantially linear and have a weight average molecular weight of at least 1000.

It has been presently found that certain salicylaldimine late transition metal chelates can provide catalyst systems for the homopolymerization of ethylene and copolymerization of ethylene and functionalized olefins to provide high molecular weight, substantially linear polymer products. The catalyst of the present invention can be represented by the following general formula:

(I)
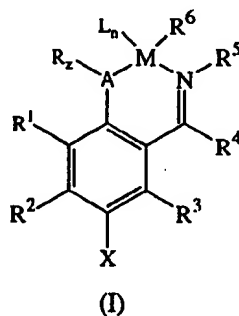
wherein

R represents a C_1-C_{11} alkyl, aryl, or substituted aryl provided z is 1 when A is nitrogen and z is 0 when A is oxygen or sulfur;

R^1 represents a hydrogen atom, C_1-C_{11} alkyl (preferably C_1-C_5 and most preferably tert-butyl); aryl,

such as phenyl, biphenyl, terphenyl, naphthyl, anthracyl, phenanthracyl and the like; substituted aryl wherein the substitution group is selected from C_1-C_6 alkyl, perfluoroalkyl, nitro, sulfonate, or halo group; arylalkyl, such as toluyl and the like; halo, such as chloro, bromo, and the like; nitro group; sulfonate group; siloxyl (-OSiA, where A is selected from phenyl or C_1-C_4 alkyl such as isopropyl or butyl and the like); or a hydrocarbyl terminated oxyhydrocarbylene group, $-(BO)_z R^7$, wherein each B independently represents a C_1-C_4 (preferably C_2-C_3) alkylene group or an arylene group (preferably phenyl and especially the B group adjacent to the basic structure to which the R^1 is bonded); R^7 represents a C_1-C_{11} (preferably a C_1-C_3) hydrocarbyl group such as an alkyl or an unsubstituted or substituted aryl group, such as phenyl, biphenyl, naphthyl and the like, alone or substituted with one or more C_1-C_6 alkyl, and z is 1 to 4. R^1 is preferably a steric bulky group selected from aryl, substituted aryl or a branched C_3-C_6 alkyl group or an alkoxyalkyl group and, most preferably, phenyl, anthracyl, phenanthracyl, terphenyl or t-butyl:

R^2 represents hydrogen atom, aryl, substituted aryl, C_1-C_{11} alkyl, halogen atom or R^1 and R^2 can, together provide a hydrocarbylene or substituted hydrocarbylene which forms a carbocyclic ring which may be non-aromatic or aromatic; R^2 is preferably hydrogen or, taken with R^1 as a carbocyclic ring group:

R^3 represents hydrogen:

R^4 represents hydrogen atom, a C_1-C_{11} alkyl, an aryl group such as a phenyl or a substituted aryl group such as 2,6-dimethylphenyl or the like, and is preferably selected from hydrogen,

R^5 represents a C_1-C_{11} alkyl group (preferably a C_4-C_8 alkyl group) such as methyl, ethyl, propyl, t-butyl, and

the like, a cycloalkyl group such as cyclohexyl and the like, an aryl group, such as phenyl, biphenyl, naphthyl or the like, or a substituted aryl having one or both ortho positions of the aromatic group (especially the phenyl group) substituted with a C_1-C_4 alkyl and/or the para position (with respect to the N-R^5 bond) substituted with a hydrogen atom, nitro, trifluoromethyl, halogen atom, methoxy, or C_1-C_4 alkyl or fused or unfused aryl, sulfonate, or a hydrocarbyl terminated oxyhydrocarbylene group -(BO)$_x$$R^7$ as defined in R^1 above. R^5 is preferably a t-butyl or a cycloalkyl such as adamantyl, or a 2,6-di(C_1-C_4 alkyl)phenyl group and most preferably 2,6-diisopropylphenyl or 2,6-diisopropyl-4-nitrophenyl:

R^1 and R^5 can, together, form an oxyhydrocarbylene chain, e.g., -(BO)$_m$B- wherein each B independently represents a C_1-C_4 alkylene group or an arylene group and m is an integer of from 2 to 5 preferably 3-5;

n is an integer of 0 or 1;

R^6 represents, when n is 1, an unsubstituted or substituted aromatic group, such as phenyl which is preferably unsubstituted, a C_1-C_{11} alkyl (preferably a C_1-C_5 alkyl and most preferably methyl), a hydrogen atom or halogen atom (preferably chloro or bromo), or when n is 0, R^6 repesents an allyl or substituted allyl group wherein the substitution can be selected from a halogen atom, a nitro group or a sulfonate group:

L represents a coordination ligand such as triphenylphosphine, tri(C_1-C_6 alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, trialkylamine, arylamine such as pyridine, C_2-C_{20} alkene such as octene, decene, dodecene, allyl and the like, a substituted alkene wherein the substitution group may be selected from a halogen atom (preferably chloro), an ester group, a C_1-C_4 alkoxy group,

an amine group (-NR$_2$ wherein each R is hydrogen, or a C$_1$-C$_3$ alkyl), carboxylic acid or its alkali metal salt, di(C$_1$-C$_3$)alkyl ether, tetrahydrofuran, a nitrile such as acetonitrile and the like:

5   X represents any electron withdrawing group such as NO$_2$, halo (chloro, bromo and the like), persulfonate (SO$_3^-$), sulfonyl ester (SO$_2$R), carboxyl (COO$^-$), a perfluoroalkyl or a hydrogen atom. The sulfonate or carboxylate is associated with an alkali or alkaline

10   earth metal cation. Less preferably, X may represent an electron donating group such as alkoxy:

       M represents one of the transition metals, that is a Group IV or VIII transition metal selected from Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state or

15   Ti, Zr, Hf in the +4 oxidation state and preferably a late transition metal selected from iron, cobalt, nickel or palladium and most preferably either nickel or palladium:

       A represents oxygen, sulfur or nitrogen.

20   The present invention provides a catalyst which contains sterically bulky groups both above and below as well as within the plane of orientation with respect to the transition metal of the complex. It is believed, though not meant to be a limitation of the invention,

25   that the steric and electronic configuration of the presently achieved complex provides the following desired characteristics:

       (1)   it utilizes late transition metals (preferably Ni or Pd) to provide high resistance to deactivation by

30   oxygenated species;

       (2)   it contains certain bidentate, chelating ligand groups which are believed to enhance the selectivity-controlling effect in the polymerization of ethylene and of α-olefins;

(3)   it contains groups of extreme steric bulk which provide shielding or partial shielding of the axial faces of the transition metal (II) square planar complexes and thereby it is believed, retards associative displacement and chain transfer during the polymerization; and

(4)   the steric bulk which is within the plane of the transition metal (II) square planar complex may inhibit chain migration processes and thereby cause substantially linear polymerization.

(5)   the steric bulk which is within the plane of the transition metal (II) square planar complex may promote dissociation of the ancillary ligand, L, and thereby result in an increase in the number of active polymerization sites.

The catalysts (I) are most preferably those having bulky substituents, such as aryl as, for example, terphenyl, anthracenyl, phenanthracenyl and the like and substituted aryl groups such as 2,6-diisopropylphenyl, in the R^1 and/or R^5 positions and further may have an electron-withdrawing group in the X position or as a substituent of the R^1 and/or R^5 group, preferably when such groups are aryl or substituted aryl type groups.

The catalyst (I) of the present invention may further contain an ether or polyether group as part of structure of the subject salicylaldimine ligand. The incorporation of such group(s) can be made at R^1 and/or at R^5 or as an oxyhydrocarbylene chain between R^1 and R^5 such that a hydrocarbon moiety of said oxyhydrocarbylene is directly bonded to the nitrogen atom at R^5 and to the aromatic ring at R^1. Such catalysts provide enhanced catalytic activity over catalyst (I) absent said group(s) and do not need the use of adjunct agent or Lewis base additive, as described herein below.

Synthesis of the precursor ligands can be achieved
by reacting the appropriate salicylaldehyde (having
desired substituent groups on the phenyl ring) with a
primary amine (R^5NH_2), such as 2,6-diisopropylaniline or

5   2,6-diisopropyl-4-nitroaniline and the like. The
reaction can be carried out in solution, such as a C_1-C_5
alcohol (e.g. methanol, ethanol or the like) or aromatic
compound (e.g., benzene, toluene or the like). The
reaction is preferably carried out at temperatures of

10   from about 15°C to 80°C (most preferably at from 15 to
25°C) for a period of from one to twenty hours (most
preferably from 10 to 12 hours). The reaction is carried
out at atmospheric pressure and in the presence of a
catalytic amount of an organic acid, such as formic acid

15   or acetic acid to provide the salicylaldimine ligand (IV)
according to the equation below:

(II)   (IV)

20   The bidentate ligand (IV) can be deprotonated using a
lithium alkyl or an alkali metal hydride (e.g., NaH being
preferred), as illustrated herein below) to form the
alkali metal salt (V). The deprotonation is carried out
at low temperatures such as about 0° to 30°C (preferably

25   0° to 10°C) at normal atmospheric pressure and in the
presence of an inert solvent, such as tetrahydrofuran,
dialkyl ether, C_5-C_{10} hydrocarbon, dioxane and the like.

The reaction normally is completed in a short period, such as from about 5 to 30 minutes. The alkali metal salt (V) can then be reacted with a late transition metal coordination compound of the type $R^6(L)_2MY$, wherein each R^6 and L are as defined above, and Y represents a halogen atom, as for example bis(triphenylphosphine) phenyl nickel chloride, and the like. This reaction may be conducted in an inert solvent, such as tetrahydrofuran, dialkyl ether, C_5-C_{10} hydrocarbon, and the like at temperatures of from about 10 to 90°C (preferably 10° to 30°C) for periods of from one to fifteen hours (normally 10-15 hours) to provide catalyst (I) as follows:

$$(IV) \; + \; QH \; \longrightarrow$$

$$\begin{array}{c} R_z{\diagdown}_{A \cdot Q^+} \quad N{\diagup}^{R^5} \\ R^1{\diagdown} \quad \quad \quad \diagup{R^4} \\ R^2{\diagup} \quad \quad {\diagdown}R^3 \\ X \end{array} \quad \xrightarrow{R^6L_2MY} \quad (I)$$

(V)

R in formulas II and IV each independently represents hydrogen atom, a C_1-C_{11} alkyl, aryl, or substituted aryl provided that R represents at least one hydrogen atom and z is 1 when A is oxygen or sulfur and z is 2 when A is nitrogen. R and z in formula V represents those groups as defined with respect to formula I above. Each of the remaining symbols R^1, R^2, R^3, R^4, R^5, R^6, M, Y, L and X represent the groups defined above with respect to catalyst I.

In the above, the R^1 may be hydrogen but preferably is a bulky group which provides a steric shield of the transition metal's equatorial face by being well-

positioned in the plane of the transition metal complex
as well as some bulk in the axial face. For example, R^1
is preferably an aryl, such as phenyl, biphenyl,
terphenyl, naphthyl, anthracenyl or phenanthracenyl, or
nitro-substituted aryl, or a bulky alkyl, such as a tert-
butyl group. Such substituted salicylaldehydes (II) are
readily formed by formylation of an appropriately
substituted phenol. This is conventionally accomplished
by reacting the substituted phenol with an aldehyde
source, such as formaldehyde (e.g., paraformaldehyde,
1,3,5-trioxane) or dimethylformamide in the presence of
stannous chloride catalyst according to the procedures
described by Casirighi et al in J. Chem. Soc. Perkins
Trans. I, 1980, 1862-5, the teachings of which are
incorporated herein by reference in its entirety.

As indicated above, R^1 may be selected from
sterically bulky groups other than hydrocarbyl groups as,
for example, siloxane groups. Such substitution can be
readily accomplished by using 2,3-dihydroxybenzaldehyde
as the starting material II to form the Schiff base
aldimine compound IV. The 3-position hydroxyl group can
then be converted to a siloxy group by reaction with the
appropriate aryl, alkyl or mixed substituted silyl halide
as, for example triisopropyl silyl chloride, diphenyl-t-
butyl silyl chloride, triphenyl silyl chloride and the
like. Deprotonation and reaction with transition metal
coordination compound of the type $R^6(L)_x MY$ provides the
desired catalyst compound I in the manner described
above.

As defined above, R^1 and R^5 may each independently be
selected from a hydrocarbyl terminated oxyhydrocarbylene
containing group. Such groups may be represented as
$-(BO)_x R^7$ wherein each B independently represents a C_1-C_4
(preferably a C_2-C_3) alkylene group or an arylene group

and R^7 represents a C_1-C_{11} (preferably C_1-C_3) hydrocarbyl
group such as alkyl, an aryl, an alkaryl, or an aralkyl
group and z represents an integer of 1 to 4. Such
oxyhydrocarbylene group may be made part of compound I by
mono-alkylation of 2,2'-dihydroxybiphenyl at one OH group
with bromoethyl ether, followed by formylation (with an
aldehyde source) of the other phenolic ring adjacent to
the OH, followed by imine formation and finally
metallation with $R^6(L)_zMY$ in the manner described
previously.

Further, it has been found that desired catalyst can
be in the form of compound (I) when the aryl group is
substituted with an electron withdrawing group X, as
defined above. For example, the salicylaldehyde may be
substituted with a nitro, halo, trifluoromethyl,
sulfonate, sulfonyl or carboxyl group in the 5-position.
Some of the substituted salicylaldehydes are commercially
available. They may be further reacted with the
substituted aniline or aniline derivative as described
above to provide the bidentate ligand IV. The ligand is
then formed into the transition metal complex I, in the
manner described above.

It has been found that substituted salicylaldimine
complexes of late transition metals described above
provide catalytic activity for olefin (e.g., ethylene)
polymerization and provide substantially linear product
having a low degree of branching. These complexes are
neutral compounds and, as such do not require the
presence of organo aluminum or partially hydrolyzed
organo aluminum compounds or other reducing agent to
cause activation of the complex towards olefin insertion
reaction and polymerization. However, organo aluminum
and hydrolyzed organo aluminum compounds, such as methyl
alumoxane or trialkyl aluminum compounds and the like,

may be present and are preferably present when R^6 is halogen. Compounds I are a new family of complexes of single-site catalysts.

The subject catalysts may be used as the sole catalyst (this is especially acceptable when the bulky group R^1 is large such as phenyl, biphenyl, terphenyl, anthracenyl, phenanthracenyl, nitro-substituted aryl or the like) or may be used in combination with an adjunct agent and/or a Lewis base (preferred). The adjunct agent comprises known phosphine sponge material capable of facilitating phosphine (ligand L) dissociation and trapping of free phosphine. Such catalyst composition adjunct agents are, for example, bis(cyclooctadiene)-nickel, tris(pentafluorophenyl) boron, 9-borabicyclo[3.3.1]nonane (9-BBN), methyl iodide, and the like.

It has unexpectedly been found that the subject catalyst provides an enhanced catalyst composition when combined with a Lewis base as, for example ethers, esters, aldehydes, ketones, alcohols, amides, organic carbonates, organonitro compounds, or mixtures thereof and even water. It is commonly believed that organometallic catalysts should be combined with Lewis acid compounds to provide effective catalyst systems and that water acts as a poison to such catalysts. In contrast to the present finding, it has been previously deemed important to use conventional single site catalysts, such as metallocene catalysts, in the absence of moisture or other oxygenated compounds in order to provide an effective catalyst system.

The Lewis base additives found useful in forming a catalyst composition with the catalyst of compound I or V comprise ether compounds, such as dialkyl ethers where each alkyl group is independently selected from a C_1-C_{18}

alkyl, preferably a C_1-C_5 alkyl group as, for example,
diethyl ether, methyl ethyl ether, diisopropyl ether,
ethyl propyl ether, dibutyl ether and the like; vinyl
ethers as, for example, ethyl vinyl ether; aryl ethers
as, for example, dibenzyl ether, diphenyl ether,
dinaphthyl ether and the like, mixed ethers as, for
example, amyl phenyl ether, methyl benzohydryl ether,
benzyl phenyl ether, anisole, phenetole and the like.
The ether additive may also be selected from cyclic
ethers as, for example, tetrahydrofuran, dioxane-1,4,
dioxane-1,3; crown ethers such as 18-crown-6, 14-crown-5,
12-crown-4 and the like as well as polyethers such as
dimethoxyethane, diglyme, triglyme, pentaglyme, or
polyoxyalkylenes as, for example, polyoxyethylene
(preferably lower molecular weight polymers which are
miscible in the polymerization solvent used).

The above ethers, especially the alkyl and/or aryl
group containing ethers and cyclic ethers described
above, and most preferably dialkyl ether (diethyl ether)
and low molecular weight polyethers (dimethoxy ethane),
have been found to be effective solvents or co-solvents
for use in the polymerization process when the subject
catalyst of compound I or compound V is used, as
described herein below.

The Lewis base may be selected from an organic ester
represented by the formula

$$R^9\overset{\displaystyle O}{\overset{\|}{C}}-OR^9$$

wherein each R^9 is independently selected from a C_1-C_{11}
alkyl group, preferably a C_1-C_5 alkyl group as, for
example, ethyl acetate, propyl acetate, hexyl acetate,

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ethyl butyrate, propyl butyrate, ethyl caproate, ethyl caprylate, ethyl laurate and the like.

Further, aldehydes and ketones have been found useful as a Lewis base additive in forming the subject catalyst composition. They may be represented by the formula

$$R^{10} \overset{\overset{\displaystyle O}{\|}}{C} R^{11}$$

wherein R^{10} represents a C_1-C_{12} hydrocarbyl selected from unsubstituted or substituted (e.g., carbonyl) alkyl, aryl, alkaryl or aralkyl groups and R^{11} represents a hydrogen atom or an R^{10} group, which is independently selected. For example, the aldehyde or ketone may be selected from acetone, propanone, butyrone, 4-heptanone, 2,4-pentanedione and the like, as well as cyclic ketones such as cyclohexanone, 1,4-cyclohexanedione and the like, or an aldehyde such as acetaldehyde, capraldehyde, valeraldehyde and the like.

Still further, an alcohol can be used as the Lewis base additive in forming the subject catalyst composition. They may be selected from monohydric or polyhydric alcohols including, for example, alcohols having hydrocarbyl moiety composed of a C_1-C_{12} (preferably C_1-C_3) alkyl, aryl (e.g., phenyl or benzyl), alkaryl and aralkyl groups. Examples of such alcohols include methanol, ethanol, propanol, isopropanol, butanol, t-butanol, 2-pentanol, 3-hexanol, glycol, 1,2,3-propanetriol, phenol, phenethyl alcohol, para-methyl phenol and the like.

Amides can be used as the Lewis base additive in forming the subject catalyst composition. The amides may be represented by the formula

$$\begin{matrix} & O \\ & \| \\ R^{12} & C-NR^{13}R^{14} \end{matrix}$$
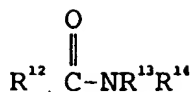
wherein R^{12} and R^{13} each independently represent a C_1-C_{11} hydrocarbyl, R^{14} represents hydrogen or a C_1-C_{11} hydrocarbyl. R^{13} and R^{14} are, preferably, independently selected from a C_1-C_3 alkyl group.

Nitroalkanes and nitroaromatics have also been found to be useful as a Lewis base additive in forming the subject catalyst composition. The nitroalkanes may be a mono (preferred) or poly nitro compound formed with a C_1-C_{11} (preferably a C_1-C_3) alkyl group. The aromatic nitro should be a mono nitro compound such as nitrobenzene and the like.

It has been unexpectedly found that the subject catalyst composition may contain small amounts of water and that the presence of water does not destroy the activity of the catalyst of the subject invention. Thus, unlike most organometallic catalysts useful in olefin polymerization, the presently described catalyst can be used in the presence of small amounts of moisture to provide a catalyst composition which can remain active in the polymerization of olefins or mixtures of olefins and functional olefin monomer(s).

The amount of the Lewis base (except water) additive can be substantially any amount desired with from 10^0 to 10^4 times the amount of compound I or V on a molar basis being preferred and most preferred, from 10^1 to 10^3 times the molar amount of catalyst when ether or low molecular weight polyether is the Lewis base used and from 10^0 to 10^2 the molar amount of catalyst when other Lewis bases are used. In the case of water, the molar ratio of water to compound I or V which may be present can range from 0 to about 10^2, preferably from 0 to 10^1.

This invention concerns processes for making
polymers, comprising, contacting the subject catalyst
composition with one or more selected olefins or
cycloolefins, alone or optionally with a functional α-
olefin such as a carboxylic acid of the formula
$CH_2=CH(CH_2)_mCOOH$, a carboxylic acid ester of the formula
$CH_2=CH(CH_2)_mCO_2R^7$ or $CH_2=CHOCOR^7$, an alkyl vinyl ether of the
formula $CH_2=CH(CH_2)_mOR^7$, vinyl ketones of the formula
$CH_2=CH(CH_2)_mC(O)R^7$, a vinyl alcohol of the formula
$CH_2=CH(CH_2)_mOH$, or a vinyl amine of the formula
$CH_2-CH(CH_2)_mNR^8{}_2$, wherein m is an integer of 0 to 10 and R^7
is a C_1-C_{10} hydrocarbyl group, aryl or substituted aryl
group (preferably methyl) and R^8 is independently selected
from hydrogen or an R^7 group; a functional cycloolefin,
such as functionalized norbornene wherein the functional
group is an ester, alcohol, carboxylic acid, halogen
atom, a primary, secondary or tertiary amine group or the
like; or unsaturated dicarboxylic acid anhydride or
carbon monoxide or the like and other selected monomers
such as vinyl halides. The "polymerization process"
described herein (and the polymers made therein) is
defined as a process which produces a polymer with a
molecular weight (Mw) of at least about 1000.

The subject catalysts may generally be written as

(I)
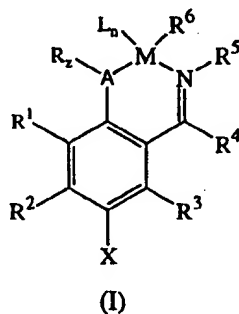
wherein each symbol R, R^1, R^2, R^3, R^4, R^5, R^6, L, M, A and X
are defined above. Preferably M is Ni(II) or Pd(II).

Alternately, the catalytic polymerization of the
present invention can be carried out by contacting one or
more selected olefins or cycloolefins alone or optionally
with a functional olefin monomer, as described above with
a catalyst composition formed in-situ and composed of one
or more bidentate ligand (V) described above in
combination with a transition metal (M) organic complex,
$R^6(L)_nMY$. The ligand (V) and complex should be used in
about a 1:1 molar ratio. In a preferred embodiment of
the present invention, the bidentate ligand V is combined
with a transition metal organic complex of the formula
$R^6(L)_nMY$ in about a 1:1 molar ratio in the presence of
olefin and/or cycloolefin alone or optionally with a
functional olefin monomer. The catalyst composition
composed of ligand (V) and transition metal organic
complex may further contain a phosphine sponge and/or a
Lewis base additive, such as those described above, or an
organo aluminum or hydrolyzed organo aluminum compound or
mixtures thereof as described above with respect to
catalyst compositions composed of compound (I) which have
a halogen as R^6.

In all catalysts and precursor bidentate ligands,
described herein, it is preferred that R^1 and R^5 are each
independently a sterically bulky hydrocarbyl. In one
form it is especially preferred that R^1 and R^5 are each
independently aryl or substituted aryl groups. In
another form, it is preferred that R^1 and/or R^5 be
independently selected from a hydrocarbyl terminated
oxyhydrocarbylene containing group, as described above.
It is also preferred that R^1 and R^2 are each taken
together to provide a hydrocarbylene which forms a
carbocyclic ring. It is further preferred that X, when

present, be an electron-withdrawing group such as nitro, trifluoromethyl, sulfonate, sulfonyl or carboxylate and the likes thereof. It is preferred that when R^5 is a substituted aryl, the 4 position of the aryl (with respect to the N- bond) be either hydrogen or nitro.

When using I or V as a catalyst in the manner described above, it is preferred that R^2, R^3 and R^4 are hydrogen or methyl, unless R^2 is, when taken together with R^3, a C_4-C_{10} carbocyclic group which may or may not be aromatic. It is also preferred that either or both R^1 and R^5 are biphenyl, terphenyl, anthracenyl, phenanthracenyl, 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 4-methylphenyl, 2-isopropyl-6-methylphenyl, phenyl, 2,4,6-trimethylphenyl, 2-t-butylphenyl, 2-t-butyl-4-methylphenyl, 2,6-diisopropyl-4-nitrophenyl, and 10-nitroanthracenyl.

The structure of the ligand associated with compound I or compound V may influence the polymer microstructure and polymer molecular weight. For example, it is preferred that R^1 be a bulky aryl or substituted aryl group. Complexes with R^1 of this type generally produce higher molecular weight and more linear polymer product for any given set of conditions. The catalyst or the catalyst composition of I or V with the phosphine sponge adjunct and/or organo aluminum compound adjunct, or with the Lewis base additive or mixtures of adjunct and Lewis base when optionally used, are contacted, usually in the liquid phase, with ethylene or other olefin ($RCH=CH_2$), and/or 4-vinylcyclohexane, 4-vinylcyclohexene, cyclopentene, cyclobutene, substituted norbornene, or norbornene. The liquid phase may include a compound added just as a solvent and/or may include the monomer(s) itself and/or may comprise the Lewis base (especially an ether compound) in the liquid phase at reaction

conditions. When an adjunct is used, the molar ratio of
adjunct to compound I or V is from about 0.001:1 to 15:1,
preferably about 0.01:1 to about 8:1, and most preferably
from 0.1:1 to 3:1. The temperature at which the

5   polymerization is carried out is from about -100°C to
about +200°C, preferably about -20°C to about +100°C and
most preferably between about 0°C and 90°C. All ranges of
temperatures being covered by this teaching. The
pressure at which the polymerization is carried out is

10   not critical, atmospheric pressure to about 100 MPa, or
more, being a suitable range. The pressure may affect
the yield, molecular weight and linearity of the
polyolefin produced, with increased pressure providing
more linear and higher molecular weight polymer product.

15   Preferred alpha-olefins and cyclic olefins in the
polymerization are one or more of ethylene, propylene, 1-
butene, 2-butene, 1-hexene, 1-octene, 1-pentene, 1-
tetradecene, norbornene, and cyclopentene, with ethylene,
propylene, cyclopentene and norbornene being more

20   preferred. Ethylene (alone as a monomer) is especially
preferred.

           The polymerization may be run in the presence of
various liquids. The solvent in which the polymerization
may be conducted can be selected from (i) the monomer(s),

25   per se or (ii) any organic compound which is liquid under
the reaction conditions and is substantially inert to the
reactants and product, or (iii) a Lewis base additive
(except water which, when used, should be present in
limited amounts) which is liquid under the reaction

30   conditions, or mixtures thereof. Particularly preferred
are aprotic organic liquids or organic ethers or mixtures
thereof. The catalyst system, monomer(s), and polymer
may be soluble or insoluble in these liquids, but
obviously these liquids should not prevent the

polymerization from occurring. Suitable liquids include
alkanes, cycloalkanes, halogenated hydrocarbons, ethers,
and aromatic and halogenated aromatic hydrocarbons.
Specific useful solvents include hexane, heptane,

5   toluene, xylenes, and benzene, methylene chloride, ethyl
ether, dimethoxyethane, tetrahydrofuran and crown ethers.
The catalyst compositions of the present invention
cause polymerization of one or more alpha-olefin, with
functional olefins such as those described herein above.

10   When carbon monoxide is used as a comonomer, it forms
alternating copolymers with the various alpha-olefins.
The polymerization to form the alternating copolymers is
carried out with both CO and the olefin simultaneously
present in the process mixture, and in the presence of

15   the present catalyst composition.
The catalyst of the present invention may also be
supported on a porous solid material (as opposed to just
being added as a suspended solid or in solution), for
instance on silica gel, zeolite, crosslinked organic

20   polymers such as styrene-divinylbenzene copolymer and the
like. By supported is meant that the catalyst may simply
be carried physically on the surface of the porous solid
support, may be adsorbed, or may be carried by the
support by other means.

25   In many of the polymerizations, certain general
trends may occur, although for all of these trends there
are exceptions. Pressure of the monomers (especially
gaseous monomers such as ethylene) has an effect on the
polymerizations in many instances. Higher pressure often

30   reduces branching and extends polymer chain length,
especially in ethylene containing polymers. Temperature
also affects these polymerizations. Higher temperature
usually increases branching.

In general, the period of time during which the
catalysts of compound I or the catalyst composition
having compound V remains active can be extended greatly
based on a particular ligand structure, polymerization
temperature, or type of Lewis present. Catalyst lifetime
is long when Lewis base such as ether or dimethyoxyethane
is present, co-catalyst adjunct is absent, and R^1 is a
bulky aryl or substituted aryl group.

When the polymer product of the present invention is
a copolymer of functionalized group containing monomer,
the functional group may be further used to cross-link
the polymer. For example, when copolymers of an olefinic
carboxylic acid or olefinic ester and an alpha-olefin are
made, they may be crosslinked by various methods known in
the art, depending on the specific monomers used to make
the polymer. For instance, carboxyl or ester containing
polymers may be crosslinked by reaction with diamines or
with diisocyanates to form bisamides. The carboxyl
groups may also be neutralized with a monovalent or
divalent metal containing base (e.g., NaOH, CaO) to form
ionomeric or pseudo-crosslinked polyolefin copolymer.

The resultant polymers formed according to the
present invention, especially those of ethylene homo or
copolymers may have varying degrees of branching in the
polymer. Branching may be determined by NMR spectroscopy
(see the Examples for details), and this analysis can
determine the total number of branches, the branching
distribution and to some extent the length of the
branches. Herein the amount of branching is expressed as
the number of branches per 1000 of the total methylene (-
CH_2-) groups in the polymers, with one exception.
Methylene groups that are in an ester grouping, i.e., -
CO_2R; a ketone group, i.e., -C(O)R are not counted as part
of the 1000 methylenes. For example, ethylene

homopolymers have a branch content of about 0 to about
150 branches per 1000 methylene groups, preferably about
5 to about 100 and most preferably about 3 to about 70
branches per 1000 methylene groups. These branches do
not include polymer end groups. Alternately, branch
content can be estimated from correlation of total
branches as determined by NMR with polymer melting point
as determined by differential scanning calorimetry.

The polymers formed by the present invention may be
mixed with various additives normally added to elastomers
and thermoplastics [see EPSE (below), vol. 14, p. 327-
410] which teaching is incorporated herein by reference.
For instance reinforcing, non-reinforcing and conductive
fillers, such as carbon black, glass fiber, minerals such
as silica, clay, mica and talc, glass spheres, barium
sulfate, zinc oxide, carbon fiber, and aramid fiber or
fibrids, may be used. Antioxidants, antiozonants,
pigments, dyes, slip agents, antifog agents, antiblock
agents, delusterants, or compounds to promote
crosslinking may be added. Plasticizers such as various
hydrocarbon oils may also be used.

The polymers formed by the present invention may be
used for one or more of the applications listed below.
In some cases a reference is given which discusses such
uses for polymers in general. All of these references
are hereby included by reference. For the references,
"U" refers to W. Gerhartz, et al., Ed., Ullmann's
Encyclopedia of Industrial Chemistry, 5th Ed. VCH
Verlagsgesellschaft mBH, Weinheim, for which the volume
and page number are given, "ECT3" refers to the H. F.
Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical
Technology, 4th Ed., John Wiley & Sons, New York, "ECT4"
refers to the J. I. Kroschwitz, et al., Ed., Kirk-Othmer
Encyclopedia of Chemical Technology, 4th Ed., John Wiley

& Sons, New York, for which the volume and page number
are given. "EPST" refers to H. F. Mark, et al., Ed.,
Encyclopedia of Polymer Science and Technology, 1st Ed.,
John Wiley & Sons, New York, for which the volume and
page number are given, "EPSE" refers to H. F. Mark, et
al., Ed., Encyclopedia of Polymer Science and
Engineering, 2nd Ed., John Wiley & Sons, New York, for
which volume and page numbers are given, and "PM" refers
to J. A. Brydson, ed., Plastics Materials, 5th Ed.,
Butterworth-Heinemann, Oxford, UK, 1989, and the page is
given. In these uses, a polyethylene, polypropylene and
a copolymer of ethylene and propylene are preferred.

1. The polyolefins herein are especially useful in
blown film applications because of their particular
rheological properties (EPSE, vol. 7, p. 88-106). It is
preferred that these polymers have some crystallinity.

2. The polymers are useful for blown or cast films
or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p
843-856; PM, p. 252 and p. 432ff). The films may be
single layer or multilayer, the multilayer films may
include other polymers, adhesives, etc. For packaging
the films may be stretch-wrap, shrink-wrap or cling wrap
and may also be heat sealable. The films are useful for
many applications such as packaging foods or liquids,
geomembranes and pond liners. It is preferred that these
polymers have some crystallinity.

3. Extruded films or coextruded films may be
formed from these polymers, and these films may be
treated, for example by uniaxial or biaxial orientation
after crosslinking by actinic radiation, especially
electron beam irradiation. Such extruded films are
useful for packaging of various sorts. The extruded
films may also be laminated to other films using
procedures known to those skilled in the art. The

laminated films are also useful for packaging of various
sorts.

4.   The polymers, particularly the elastomers, may
be used as tougheners for other polyolefins such as
polypropylene and polyethylene.

5.   Tackifiers for low strength adhesives (U, vol.
A1, p 235-236) are a use for these polymers. Elastomers
and/or relatively low molecular weight polymers are
preferred.

6.   An oil additive for smoke suppression in
single-stroke gasoline engines is another use.
Elastomeric polymers are preferred.

7.   The polymers are useful as base resins for hot
melt adhesives (U, vol. A1, p 233-234), pressure
sensitive adhesives (U, vol. A1, p 235-236) or solvent
applied adhesives. Thermoplastics are preferred for hot
melt adhesives.

8.   Base polymer for caulking of various kinds is
another use. An elastomer is preferred. Lower molecular
weight polymers are often used.

9.   Wire insulation and jacketing may be made from
any of the polyolefins (see EPSE, vol. 17, p. 828-842).
In the case of elastomers it may be preferable to
crosslink the polymer after the insulation or jacketing
is formed, for example by free radicals.

The following examples are provided herein below for
illustrative purposes only and are not meant to be a
limitation on the scope of the invention. All parts and
percentages are by weight unless otherwise indicated.

Example I
HOC_6H_4-o-C(H)=N-2,6-C_6H_3(i-Pr)$_2$
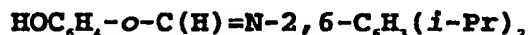
To a methanol (25 mL) solution of salicylaldehyde
(10g, 82 mmol) was added formic acid (1 mL) and 2,6-

diisopropylaniline (21 g, 120 mmol). The resulting
mixture was stirred for 1 hour. After this time, a
yellow solid precipitated out of solution. The solid was
collected by filtration through a glass frit and washed

5   with methanol (2 X 10 mL) to yield 21 g (90%) of a yellow
solid. ^{1}H NMR(C_6D_6): δ1.24 (d, 12H, J_{HH}=6.94 Hz), 3.07
(septet, 2H, J_{HH}=6.94 Hz), 7.02-7.48 (m, 7H), 8.39 (s,
1H), 13.12 (s, 1H); ^{13}C NMR (C_6D_6): δ23.5, 28.2, 117.2,
119.1, 123.3, 125.6, 132.5, 133.3, 138.8, 146.4, 161.3,

10   167.0.

Example II

[OC$_6$H$_4$-o-C=N-2,6-C$_6$H$_3$(i-Pr)$_2$]Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the

15   product of Example I (0.59 g, 1.5 mmol) and
bis(triphenylphosphine)nickel(phenyl) chloride (1.0 g,
1.44 mmol) in benzene (20 mL). The reaction was stirred
at room temperature for 1 hour. After this time, the
reaction was filtered by cannula filtration, and the

20   filtrate was concentrated in vacuo to ~5 mL. Pentane (30
mL) was added to the reaction. A yellow-orange solid
precipitated from solution, and was isolated by cannula
filtration to yield 0.74 g (76%) of a yellow-orange
solid. ^{1}H NMR (C_6D_6): δ 1.03 (d, 6H, J_{HH}=6.84 Hz), 1.29 (d,

25   6H, J_{HH}=6.84 Hz), 4.05 (septet, 2H, J_{HH}=6.84 Hz), 6.31-7.69
(m, 27H), 7.93 (d, 1H, J_{HP}=8.80 Hz); ^{13}C NMR (C_6D_6): δ22.6,
25.5, 28.8, 117.4, 120.0, 122.8, 125.3, 126.2, 128.3,
128.6, 129.7, 130.5, 131.0, 131.5, 133.3, 133.8, 134.0,
134.4 (d, J_{CP}=9.77 Hz), 137.4, 140.1, 149.4, 159.6, 165.2;

30   ^{31}P NMR (C_6D_6): δ25.94. Anal. Calcd for $C_{43}H_{42}NNiOP$: C,
76.35; H, 6.25; N, 2.07. Found: C, 76.20; H, 6.64; N,
1.89.

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Example III
HO-(3-*t*-Bu)C$_6$H$_3$-*o*-C(H)=N-2,6-C$_6$H$_3$(*i*-Pr)$_2$
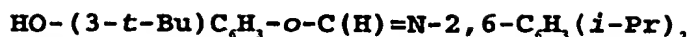
To a methanol (25 mL) solution of t-butylsalicylaldehyde (10 g, 82 mmol) was added formic acid (1 mL) and 2,6-diisopropylaniline (21 g, 120 mmol). The resulting mixture was refluxed for 10 hours. After this time, the methanol was removed by rotary evaporation to yield a dark-brown oil. The oil was loaded onto a silica gel column and eluted with 90:10 hexane:ethyl acetate to yield 24 g (90%) of a viscous, orange oil. ^{1}H NMR (C$_6$D$_6$): δ 1.24 (d, 12H, J_{HH}=6.85 Hz), 1.56 (s, 9H), 3.10 (septet, 2H, J_{HH}=6.85 Hz), 6.94-7.49 (m, 6H), 8.39 (s, 1H), 13.71 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 23.5, 28.2, 34.9, 118.3, 118.6, 123.3, 125.4, 130.5, 130.8, 137.6, 139.0, 146.4, 160.7, 167.6.

Example IV
HO-(3-Ph)C$_6$H$_3$-*o*-C(H)=N-2,6-C$_6$H$_3$(*i*-Pr)$_2$

To a methanol (15 mL) solution of 6-phenyl salicylaldehyde (2.4 g, 12 mmol) was added formic acid (0.50 mL) and 2,6-diisopropylaniline (2.8 g, 16 mmol). The resulting mixture was refluxed for 10 hours. After this time, the methanol was cooled to room temperature at which time yellow crystals precipitated from the solution. The crystals was collected by filtration and washed with methanol (2 X 10 mL) to yield 3.0 g (70%) of a yellow solid. ^{1}H NMR (C$_6$D$_6$): δ 1.01 (d, 12H, J_{HH}=6.88 Hz), 2.96 (septet, 2H, J_{HH}=6.88 Hz), 7.05-7.74 (m, 11H), 7.92 (s, 1H), 13.90 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ23.5, 28.5, 119.2, 119.3, 123.5, 125.9, 127.4, 127.7., 129.9, 130.8, 131.9, 134.7, 138.0, 138.9, 146.8, 159.4, 167.6.

Example V

[O-(3-*t*-Bu)C₆H₃-*o*-C(H)=N-2,6-C₆H₃(*i*-Pr)₂]Nickel(phenyl) (PPh₃)

In a Schlenk flask was dissolved the Na salt of the
product of Example III (2.1 g, 4.8 mmol) and
bis(triphenylphosphine)nickel(phenyl)chloride (3.1 g, 4.4
mmol) in THF (50 mL). The reaction was stirred at room
temperature for 1.5 hours. After this time, the reaction
was filtered by cannula filtration and the filtrate was
concentrated in vacuo to ~5 mL. Pentane (30 mL) was
added with vigorous stirring and the reaction was cooled
at -78°C. A yellow-orange solid precipitated from
solution, and was isolated by cannula filtration to yield
3.5 g (83%) of a yellow-orange solid. ^{1}H MNR (C₆D₆): δ
0.93 (s, 9H), 1.08 (d, 6H, J_{HH}=5.88 Hz), 1.22 (d,
6H, J_{HH}=5.88 Hz), 4.28 (septet, 2H, J_{HH}=5.88 Hz), 6.21-7.83
(m, 26H), 7.97 (d, 1H, J_{HP}=9.12 Hz); ^{13}C (C₆D₆): δ 22.7,
25.5, 28.9, 29.8, 34.6, 113.9, 120.2, 121.0, 122.8,
125.0, 125.9, 128.3, 128.5, 129.1, 129.7, 131.5, 131.8,
132.2, 133.3, 134.9 (d, J_{CP}=10.4 Hz), 137.0, 140.8, 141.9,
150.2, 166.1, 166.8; ^{31}P NMR (C₆D₆): δ 23.35. Anal. Calcd
for C₄₇H₅₀NNiOP: C, 77.06; H, 6.88; N, 1.91. Found: C,
76.93; H, 6.81; N, 1.63.

Example VI

[O-(3-Ph)C₆H₃-*o*-C(H)=N-2,6-C₆H₃(*i*-Pr)₂]Nickel(phenyl)(PPh₃)

In a Schlenk flask was dissolved the Na salt of the
product of Example IV (0.56 g, 1.6 mmol) and
bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4
mmol) in benzene (20 mL). The reaction was stirred at
reflux for 1 hour. After this time, the reaction was
filtered by cannula filtration and the filtrate was
concentrated in vacuo to ~5 mL. Pentane (30 mL) was

30

added to the vigorously stirred solution. A light-green
solid precipitated from solution, and was isolated by
cannula filtration to yield 0.84 g (89%) of a yellow-
orange solid. ^{1}H NMR (C_6D_6): δ 1.12 (d, 6H, J_{HH}=6.56 Hz),
1.21 (d, 6H, J_{HH}=6.56 Hz), 3.3 (s, 3H), 4.11 (septet, 2H,
J_{HH}=6.56 Hz), 3.29 (s, 3H), 6.18-7.80 (m, 31H), 7.99 (d,
1H, J_{HP}=9.52 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.4,
119.8, 121.1, 122.7, 125.0, 126.0, 127.4, 128.6, 129.4,
129.6, 131.7, 132.1, 134.0, 134.3, 134.4 (d, J_{CP}=9.76 Hz),
135.3, 136.8, 137.8, 140.1, 140.7, 150.0, 163.7, 166.5;
^{31}P NMR (C_6D_6): δ 21.87. Anal. Calcd for $C_{49}H_{46}NNiOP$: C,
78.20; H, 6.16; N, 1.86. Found: C, 77.69; H, 6.36; N,
1.42.

Example VII
2-(9-Phenanthrene)phenol-tetrahydropyran adduct

A solution of tetrahydropyran-protected phenol (10
g, 56 mmol) in diethyl ether (100 mL) was treated at room
temperature with BuLi (44 mL, 70 mmol) for 4.5 hours. A
solution of $MgBr_2$ was separately prepared by slowly adding
1,2-dibromoethane (5.3 mL, 62 mmol) to Mg turnings (1.6
g, 67 mmol) in diethyl ether (100 mL), and stirred for 4
hours. The Li-salt was added via cannula to the $MgBr_2$
solution to form the Grignard reagent. This solution was
added to a cooled solution (-78°C) of 9-bromophenanthrene
(9.7 g, 38 mmol) and $NiCl_2$(diphenylphosphinoethylene)
(0.62 g, 1.2 mmol). The mixture was slowly warmed to
room temperature and heated at reflux overnight. After
this time, the reaction mixture was poured through a
short silica gel column with 1:1 dichloromethane:hexane.
The solvent was removed under vacuum to leave an orange,
viscous oil. The yield of crude product was 14 g (70%).
^{1}H NMR ($CDCl_3$): δ 1.02-1.48 (m, 6H), 3.75 (m, 2H), 5.42

(d, 1H, J_{HH}=8.40 Hz), 7.20-8.81 (m, 13H); ^{13}C NMR (C$_6$D$_6$): δ
17.7, 18.3, 25.2, 30.1, 61.6, 62.0, 96.3, 96.9, 115.1,
115.4, 121.8, 121.9, 122.7, 126.1, 126.2, 126.3, 126.5,
126.7, 128.7, 129.2, 129.3, 130.1, 130.2, 130.5, 130.6,
131.5, 131.6, 131.7, 131.9.

Example VIII

2-(Phenanthrene)salicylaldehyde

To a solution of 2-(9-phenanthrene)phenol (6.8 g, 25
mmol) and 2,6-lutidine (4.6 g, 43 mmol) in toluene (50
mL) was slowly added SnCl$_4$ (0.75 mL, 6.4 mmol). The
solution was stirred at room temperature for 20 minutes.
Paraformaldehyde was added (4.3 g, 140 mmol) and the
reaction was stirred at 110°C for 12 hours. After cooling
to room temperature, the reaction mixture was poured into
water (30 mL), and adjusted to pH 1 with concentrated
HCl. The mixture was extracted with diethyl ether (500
mL), and the organic layer was washed twice with sat.
brine and dried over Na$_2$SO$_4$. The solvent was removed by
rotary evaporation to leave a yellow oil. The oil was
loaded onto a silica gel column and eluted with 9:1
hexane:ethyl acetate. The yield of product was 1.9 g
(26%). ^{1}H NMR (CDCl$_3$): δ 7.21-8.78 (m, 12H), 10.02 (s,
1H), 11.32 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 120.0, 120.6, 122.7,
123.0, 126.6, 126.9, 127.0, 128.5, 128.8, 130.5, 130.8,
131.5, 133.8, 139.1, 159.6, 196.9.

Example IX

HO-3-(9-Phenanthrene)C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$

2-(9-Phenanthrene)salicylaldehyde (1.9 g, 6.4 mmol),
2,6-diisopropylaniline (1.4 g, 7.9 mmol), and p-
toluenesulfonic acid (65 mg, 0.34 mmol) was dissolved in
benzene (27 mL). The solution was stirred at reflux

overnight. After this time, the benzene was removed
under vacuum. To the resulting oil was added hexane (100
mL) under vigorous stirring at which time a white solid
precipitated. The solid was collected by filtration
5   through a glass frit. A second crop of product was
obtained from the filtrate to yield 1.7 g (58%). ^{1}H NMR
(CDCl$_3$): δ1.22 (d, 12H, J_{HH}=6.90 Hz), 3.07 (septet, 2H,
J_{HH}=6.90 Hz), 7.14-8.90 (m, 15H), 8.46 (s, 1H), 13.45 (s,
1H); ^{13}C NMR (C$_6$D$_6$): δ23.8, 28.2, 119.0, 122.7, 123.0,
10   123.4, 125.0, 126.6, 126.8, 127.2, 128.5, 128.9, 129.3,
130.4, 130.6, 131.2, 131.7, 132.2, 135.6, 138.9, 159.3,
166.9.

Example X
15   ### 2-(Anthracene)phenol-tetrahydropyran adduct
In a three-necked, 250 mL flask under an atmosphere
of Ar was added Mg turnings (2.1 g, 87 mmol) in THF (20
mL). A few drops of 1,2-dibromoethane was added to
activate the Mg. Then a solution of the tetrahydropyran-
20   protected 2-bromophenol (22 g, 87 mmol) in THF (70 mL)
was added dropwise, and the reaction was stirred at
reflux overnight. After this time, the resulting slurry
was added by cannula to a solution of 9-bromoanthracene
(22 g., 88 mmol) and NiCl$_2$(dppe) (1.4 g, 2.6 mmol) in THF
25   (175 mL). The resulting solution was heated at reflux
for 4 days. After this time, the solvent was removed in
vacuo, and the oily residue was chromatographed on a
silica gel column with 90:10 hexane:ethyl acetate.
Removal of solvent yielded 10 g (34%) of a white
30   crystalline solid. ^{1}H NMR (CDCl$_3$): δ 0.87-1.30 (m, 6H),
3.42 (m, 1H), 3.60 (m, 1H), 5.30 (s, 1H), 7.25-8.49 (m,
13H); ^{13}C NMR (C$_6$D$_6$): δ 17.7, 24.9, 30.0, 61.6, 61.9, 96.1,
96.4, 115.3, 115.8, 121.4, 121.7, 124.7, 125.2, 126.0,

126.6, 127.1, 127.5, 127.8, 128.2, 128.6, 129.0, 130.2,
130.3, 131.3, 132.5, 132.9, 133.9, 155.4.

<u>Example XI</u>

5   **2-(Anthracene)salicylaldehyde-tetrahydropyran adduct**

To a diethyl ether (250 mL) solution of the
tetrahydropyran-protected adduct of 2-(9-anthracene)
phenol was added *n*-BuLi (28 mL, 43 mmol) dropwise. The
resulting solution was stirred at room temperature for
10   4.5 hours. After this time, the solution was cooled to -
78°C and dimethyl formamide (5.4 mL, 70 mmol) was added to
the reaction, which was allowed to warm to room
temperature. After this time, the reaction was quenched
with H_2O and extracted with diethyl ether (200 mL). The
15   organic layer was separated and dried with Na_2SO_4. The
solvents were removed by rotary evaporation to yield a
yellow solid. The solid was washed with hexane (50 mL)
and dried in vacuo to yield 5.0 g (60%) product. ^{1}H NMR
($CDCl_3$): δ 0.56-1.97 (m, 6H), 2.89 (m, 1H), 3.48 (m, 1H),
20   4.27 (m, 1H), 7.46-8.10 (m, 13H), 8.57 (s, 1H), 10.62 (s,
1H); ^{13}C NMR (C_6D_6): δ 19.5, 24.6, 29.9, 64.2, 102.4,
124.6, 125.5, 126.1, 126.2, 126.5, 127.6, 128.0, 128.4,
128.7, 130.0, 130.4, 130.8, 131.2, 131.3, 131.9, 132.9,
159.0, 191.8.

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<u>Example XII</u>

2-(Anthracene)salicylaldehyde

The tetrahydropyran-protected 2-(9-anthracene)
salicylaldehyde of Example XI (8.4 g, 22 mmol) was
30   dissolved in ethanol (75 mL) and THF (100 mL). To the
solution was added pyridinium *p*-toluenesulfonate (0.28 g,
1.1 mmol), and the reaction was stirred at reflux
overnight. The solvents were removed in vacuo to yield

6.7 g (99%) of crude product. ^{1}H NMR (CDCl$_3$): δ 7.25-8.55 (m, 13H), 10.05 (s, 1H), 11.22 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 120.0, 120.9, 125.3, 125.9, 126.1, 127.3, 127.6, 128.8, 130.3, 130.8, 131.5, 134.0, 140.4, 159.9, 196.9.

Example XIII

HO-3-(9-Anthracene)C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$

2-(Anthracene)salicylaldehyde (6.5 g, 22 mmol), 2,6-diisopropylaniline (4.6 g, 26 mmol), and p-toluenesulfonic acid (215 mg, 1.1 mmol) were dissolved in benzene (250 mL) and stirred under reflux for 3 hours in a Dean-Stark apparatus. After this time, the solvent was removed in vacuo, and the resulting residue was washed with hexane (100 mL) and methanol (20 mL), and dried in vacuo. The yield of product was 8.8 g (88%). ^{1}H NMR (CDCl$_3$): δ 1.23 (d, 12H, J_{HH}=6.90 Hz), 3.09 (septet, 2H, J_{HH}=6.90 Hz), 7.23-8.52 (m, 15H), 8.59 (s, 1H), 13.33 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 23.8, 28.2, 119.0, 119.1, 123.4, 125.2, 125.6, 125.7, 126.7, 127.0, 127.3, 128.5, 128.8, 130.5, 131.6, 132.4, 132.5, 136.8, 138.9, 146.3, 159.6, 166.8.

Example XIV

[O-3-(9-Phenanthrene)C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$]
Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the product of Example IX (0.87 g, 1.6 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.40 mmol) in benzene (20 mL). The reaction of was stirred at room temperature for 1.5 hours. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring. A

yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.92 g (75%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.08 (d, 6H, J_{HH}= 6.96 Hz), 1.19 (d, 6H, J_{HH}=6.96 Hz), 1.21 (d, 6H, J_{HH}=6.96 Hz), 1.32 (d, 6H, J_{HH}=6.96 Hz), 4.16 (septet, 2H, J_{HH}=6.96 Hz), 6.14-8.37 (m, 35H), 8.13 (d, 1H, J_{HP}=11.36 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.2, 119.9, 121.2, 122.8, 124.5, 124.7, 124.9, 125.6, 126.1, 127.2, 127.4, 128.4, 128.9, 130.5, 130.8, 131.1, 131.5, 131.8, 133.5 (d, J_{CP}=13.4 Hz), 134.7, 136.6, 137.4, 138.3, 140.7, 145.2, 146.4, 150.1, 165.2, 166.7; ^{31}P NMR (C_6D_6): δ 25.09. Anal. Calcd for $C_{57}H_{50}NNiOP$: C, 80.29; H, 5.91; N, 1.64. Found: C, 80.06; H, 6.14; N, 1.25.

Example XV
[O-3-(9-Anthracene)C_6H_3-o-C(H)-N=C-2,6-C_6H_3(i-Pr)$_2$] Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the product of Example XIII (0.53 g, 1.6 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (2.0 g, 2.9 mmol) in benzene (20 mL). The reaction was stirred at room temperature for 1.5 hours. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added with vigorous stirring and the reaction was cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.71 mg (78%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 1.14 (d, 6H, J_{HH}=6.56 Hz), 1.18 (d, 6H, J_{HH} = 6.56 Hz), 4.16 (septet, 2H, J_{HH} = 6.56 Hz), 6.17-7.83 (m, 40H), 8.15 (d, 1H, J_{HP} = 11.32 Hz); ^{13}C NMR (C_6D_6): δ 22.6, 25.6, 28.9, 114.2, 119.9, 121.2, 122.8, 124.5, 124.7, 124.9, 125.6, 126.1, 127.2, 127.4, 128.4, 128.9, 130.5, 130.8, 131.1,

131.5, 131.8, 133.5 (d, J_{CF}=13.4 Hz), 134.7, 136.6, 137.4, 138.3, 140.7, 145.2, 146.4, 150.1, 165.2, 166.7; ^{31}P NMR (C_6D_6): δ 22.99. Anal. Calcd for $C_{57}H_{50}NNiOP$: C, 80.29; H, 5.91; N, 1.64. Found: C, 79.77; H, 6.09; N, 1.49.

Example XVI

2,3-Dihydroxy,1-(2,6-diisopropyl)benzaldimine

In a round-bottom flask was dissolved 10 g (72 mmol) of 1,2-dihydroxybenzaldehyde, 2,6-diisopropylaniline (16 g, 90 mmol), and formic acid (1 mL) in methanol (20 mL). The solution was stirred vigorously for 5 minutes at which time the light yellow-brown solution became dark red, and a light orange-red solid precipitated from solution. The solid was collected by filtration through a glass frit, washed twice with cold methanol (-20°C), and dried under vacuum to yield 22 g (98%). ^{1}H NMR (CD_2Cl_2): δ 1.27 (d, 12H, J_{HH}= 6.72 Hz), 3.11 (septet, 2H, J_{HH} = 6.72 Hz), 6.93 (t, 6H, J_{HH} = 7.92 Hz), 7.04 (d, 1H, J_{HH} = 7.92 Hz), 7.15 (d, 1H, J_{HH} = 11.0 Hz) 7.29 (br s, 3H), 8.40 (s, 1H); ^{13}C NMR (CD_2Cl_2): δ 23.5, 28.4, 118.1, 118.3, 119.1, 123.2, 123.4, 126.0, 139.2, 145.4, 145.6, 149.7, 145.6, 167.1.

Example XVII

HO-3-[O-Si(^{i}PR)$_3$]C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$

In a Schlenk flask under an atmosphere of N_2 was dissolved the compound of Example XVI (3.0 g, 10 mmol), triisopropylsilylchloride (2.3 g, 12 mmol), and imidazole (0.96 g, 14 mmol) in DMF (40 mL). The reaction was stirred at room temperature for 4 hours. After this time, Et_2O (250 mL) was added, and the solution was washed twice with water (2 X 100 mL). The Et_2O layer was dried with Na_2SO_4 and concentrated on a rotary evaporator to a

yellow-orange oil. The oil was loaded onto a silica gel
column and eluted with 95:5 hexane:ethyl acetate.
Removal of solvent yielded 4.1 g (89%) of an orange oil.
^{1}H NMR (C_6D_6): δ 0.99 (d, 12H, J_{HH} = 6.86 Hz), 1.15 (d, 18H,

5   J_{HH}= 6.83 Hz), 1.29 (septet, 3H, J_{HH} = 6.83 Hz), 2.93
(septet, 2H, J_{HH} = 6.86 Hz), 6.59-7.11 (m, 6H), 7.89 (s,
1H), 13.44 (s, 1H); ^{13}C NMR (C_6D_6): δ 20.4, 23.5, 26.7,
28.4, 118.5, 119.8, 123.5, 123.8, 124.9, 125.8, 130.1,
133.4, 135.9, 138.8, 144.8, 153.5, 167.4.

10

Example XVIII

HO-3-[O-Si(Ph)$_2$(t-But)]C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$

In a Schlenk flask under an N_2 atmosphere was
dissolved the compound of Example XVI (3.0 g, 10 mmol),

15   diphenyl-t-butylsilylchloride (3.3 g, 12 mmol), and
imidazole (0.96 g, 14 mmol) in DMF (40 mL). The reaction
was stirred at room temperature for 4 hours. After this
time, Et$_2$O (250 mL) was added and the solution was washed
twice with distilled water (2 X 100 mL). The Et$_2$O layer

20   was dried with Na$_2$SO$_4$ and concentrated on a rotary
evaporator to a yellow-orange oil. The oil was loaded
onto a silica gel column and eluted with 90:10
hexane:ethyl acetate. Removal of solvent yielded 4.4 g
(83%) of an orange oil. ^{1}H NMR (C_6D_6): δ 0.98 (d, 12H, J_{HH} =

25   6.84 Hz), 1.26 (s, 9H), 2.90 (septet, 2H, J_{HH} = 6.84 Hz),
6.28 (t, 1H, J_{HH} = 7.77 Hz), 6.47 (d, 1H, J_{HH} = 7.77 Hz),
6.82 (d, 1H, J_{HH} = 7.92 Hz), 7.10 (m, 3H), 7.87 (m, 1H),
13.49 (s,1H); ^{13}C NMR (C_6D_6): δ13.3, 18.2, 23.4, 28.5,
118.8, 119.8, 123.5, 124.1, 124.9, 125.8, 138.8, 145.4,

30   146.9, 153.7, 167.4.

Example XIX

[O-3-[O-Si(^{i}Pr)$_3$]C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$] Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the product of Example XVII (0.70 g, 1.3 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (30 mL). The reaction of was stirred at room temperature for 30 minutes. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added and the reaction was cooled to -78°C and stored at this temperature for 2 days. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.70 g (57%) of a waxy, yellow-orange solid. ^{1}H NMR (C$_6$D$_6$): δ 0.84 (br s, 18H), 1.09 (d, 6H, J_{HH} = 7.32 Hz), 1.21 (d, 6H, J_{HH} = 7.32 Hz), 4.20 (septet, 2H, J_{HH} = 7.32 Hz), 6.15-7.80 (m, 30H), 7.97 (d, 1H, J_{HP} = 8.72 Hz); ^{13}C NMR (C$_6$D$_6$): δ 13.0, 18.0, 22.8, 25.5, 28.9, 113.1, 120.4, 120.7, 121.0, 122.7, 125.0, 125.9, 126.2, 129.5, 132.4, 132.8, 134.1, 134.8 (d, J_{CP} = 9.76 Hz), 136.7, 138.0, 140.7, 149.2, 150.0, 159.0, 166.0; ^{31}P NMR (C$_6$D$_6$): δ23.13.

Example XX

[O-3-[O-Si(Ph)$_2$(t-Bu)]C$_6$H$_3$-o-C(H)-N=C-2,6-C$_6$H$_3$(i-Pr)$_2$ Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the compound of Example XVIII (0.81 g, 1.3 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (30 mL). The reaction was stirred at room temperature for 1.5 hours. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30

mL) was added with vigorous stirring, and the reaction
was cooled to -25°C. A yellow-orange solid precipitated
from solution, and was isolated by cannula filtration to
yield 0.92 g (68%) of a yellow-orange solid. ^{1}H NMR
(C_6D_6): δ 0.52 (s, 9H), 1.05 (d, 6H, J_{HH}= 6.60 Hz), 1.21 (d,
6H, J_{HH} = 6.60 Hz), 4.12 (septet, 2H, J_{HH} = 6.60 Hz), 6.18-
7.75 (m, 40H), 7.94 (d,1H, J_{HP} = 9.16 Hz); ^{13}C NMR (C_6D_6): δ
18.8, 22.7, 25.5, 26.3, 28.8, 99.8, 113.1, 120.5, 121.1,
122.5, 122.9, 125.0, 126.2, 127.5, 129.6, 130.0, 132.5,
133.6, 134.9 (d, J_{CP} = 9.76 Hz), 135.7, 136.7, 140.8,
148.6, 150.0, 155.6, 158.8, 159.1, 166.2; ^{31}P NMR (C_6D_6): δ
22.78. Anal. Calcd for $C_{59}H_{60}NNiO_2PSi$: C, 75.96; H, 6.48; N,
1.50; Found: C, 75.57; H, 6.74; N, 1.03.

Example XXI

[(4S)-4,5-dihydro-2-(2'-oxidophenyl-χO)-4-isopropyloxazole-χN)]Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of
(4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole
(470 g, 1.6 mmol) and bis(triphenylphosphine)nickel
(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL).
The reaction was stirred at room temperature for 1.5
hours. After this time, the reaction was filtered by
cannula filtration, and the filtrate was concentrated in
vacuo to ~3 mL. Pentane (30 mL) was added with vigorous
stirring and the reaction was cooled to -78°C. A yellow-
orange solid precipitated from solution, and was isolated
by cannula filtration to yield 0.54 g (62%) of a yellow-
orange solid. ^{1}H NMR (C_6D_6): δ 0.24 (d, 3H, J_{HH} = 8.80 Hz),
0.63 (d, 3H, J_{HH} = 8.80 Hz), 2.24 (septet, 1H, J_{HH} = 8.80
Hz), 2.92 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ = 2.92 Hz), 3.36
(t, 1H, J_{HH} = 8.80 Hz), 3.64 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$

40

= 2.92 Hz), 6.09-7.73 (m, 29H); ^{13}C NMR (C_6D_6): δ 68.0,
74.2, 109.3, 113.1, 121.6, 122.5, 122.6, 126.3, 127.4,
127.8, 127.9, 128.3, 128.6, 129.6, 131.1, 131.5, 133.5,
133.7, 133.9, 134.5 (d, J_{CP} = 10.4 Hz), 143.4, 149.1,
5   149.5, 166.5, 168.8; ^{31}P NMR (C_6D_6): δ 28.88.

Example XXII

[(4S)-4,5-dihydro-2-(2'oxidophenyl-χO)-4-isopropyloxazole-χN)]Nickel(phenyl)(PPh$_3$)

10   In a Schlenk flask was dissolved the Na salt of
(4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole
(530 g, 1.6 mmol) and bis(triphenylphosphine)nickel
(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL).
The reaction was stirred at room temperature for 1.5
15   hours. After this time, the reaction was filtered by
cannula filtration, and the filtrate was concentrated in
vacuo to ~5 mL. Pentane (30 mL) was added with vigorous
stirring, and the reaction was cooled to -78°C. A yellow-
orange solid precipitated from solution, and was isolated
20   by cannula filtration to yield 0.71 g (78%) of a yellow-
orange solid. ^{1}H NMR (C_6D_6): δ 4.13 (d of d, 1H, J_{HH} = 8.32
Hz, $J_{HH'}$ = 8.32 Hz), 4.22 (d of d, 1H, J_{HH} = 8.32 Hz, $J_{HH'}$ =
8.32 Hz), 4.43 (t, 1H, J_{HH} = 8.32 Hz), 6.09-7.73 (m, 29H);
^{13}C NMR (C_6D_6): δ 68.0, 74.2, 109.3, 113.1, 121.6, 122.5,
25   122.6, 126.3, 127.4, 127.8, 127.9, 128.3, 128.6, 129.6,
131.1, 131.5, 133.5, 133.7, 133.9, 134.5 (d, J_{CP} = 10.4
Hz), 143.4, 149.1, 149.5, 166.5, 168.8; ^{31}P NMR (C_6D_6): δ
28.01. Anal. Calcd for $C_{39}H_{32}NNiO_2P$: C, 73.61; H, 5.07; N,
2.20. Found: C, 73.77; H, 5.24; N, 2.23.

30

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Example XXIII

HO-5-(OMe)C$_6$H$_3$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$
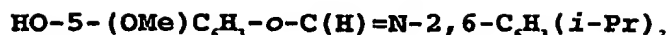
To a methanol (25 mL) solution of 4-
methoxysalicylaldehyde (10 g, 66 mmol) was added formic
acid (1.0 mL) and 2,6-diisopropylaniline (15 g, 65 mmol).
The resulting mixture was stirred at room temperature for
1 hour. After this time, the solution was stored at -25°C
for 24 hours. Yellow crystals precipitated from
solution. The crystals were filtered and washed with
-25°C methanol (2 X 20 mL) to yield 15 g (72%) of a yellow
solid. ^{1}H NMR (C$_6$D$_6$): δ 1.07 (d, 12H, J_{HH} = 8.56 Hz), 2.98
(septet, 2H, J_{HH} = 8.56 Hz), 3.29 (s, 3H), 6.60-7.16 (m,
6H), 7.86 (s, 1H), 12.89 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 23.5,
28.5, 55.3, 115.8, 118.7, 120.7, 123.5., 125.8, 138.7,
147.1, 152.7, 156.2, 167.

Example XXIV

HO-5-(NO$_2$)C$_6$H$_3$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$
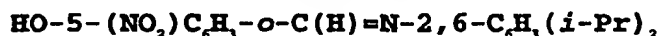
To a methanol (15 mL) solution of 4-
nitrosalicylaldehyde (10 g, 60 mmol) was added formic
acid (1.0 mL) and 2,6-diisopropylaniline (13 g, 75 mmol).
The resulting mixture was stirred at room temperature for
10 minutes. After this time, yellow crystals
precipitated from the solution. The crystals were
filtered and washed with methanol (2 X 20 mL) to yield 15
g (96%) of a yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.19 (d,
12H, J_{HH} = 6.85 Hz), 2.96 (septet, 2H, J_{HH} = 6.85 Hz), 7.14
(d, 1H, J_{HH} = 9.18 Hz), 7.23 (br s, 3H), 8.30 (d, 1H, J_{HH} =
9.18 Hz), 8.40 (s, 1H), 8.43 (s, 1H), 14.30 (s, 1H); ^{13}C
NMR (CD$_2$Cl$_2$): δ 23.6, 28.6, 118.6, 123.8, 126.6, 128.7,
128.8, 133.1, 139.1, 140.9, 145.2, 166.0, 167.4.

Example XXV

HO-3,5-Cl$_2$C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$
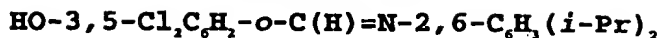
To a methanol (15 mL) solution of 4,6-dichlorosalicylaldehyde (10 g, 52 mmol) was added formic acid (1.0 mL) and 2,6-diisopropylaniline (12 g, 65 mmol). The resulting mixture was stirred at room temperature for 10 minutes. After this time, yellow crystals precipitated from the solution. The crystals were filtered and washed with methanol (2 X 20 mL) to yield 17 g (95%) of a yellow solid. ^{1}H NMR (C$_6$D$_6$): δ 0.98 (d, 12H, J_{HH} = 6.88 Hz), 2.77 (septet, 2H, J_{HH} = 6.88 Hz), 6.60-7.11 (m, 5H), 7.47 (s, 1H), 14.02 (s, 1H); ^{13}C NMR (C$_6$D$_6$): δ 23.2, 28.2, 119.6, 123.1, 123.2, 123.3, 126.2, 129.7, 132.9, 138.3, 145.4, 156.3, 165.5.

Example XXVI
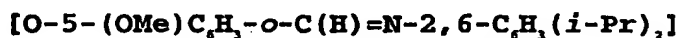
[O-5-(OMe)C$_6$H$_3$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$] Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the product from Example XXII (0.64 g, 1.6 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at room temperature for 1 hour. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the vigorously stirred solution, which was then cooled to -78°C. A yellow-orange solid precipitated from solution, and was isolated by cannula filtration to yield 0.88 g (86%) of a yellow-orange solid. ^{1}H NMR (C$_6$D$_6$): δ 1.08 (d, 6H, J_{HH} = 6.84 Hz), 1.30 (d, 6H, J_{HH} = 6.84 Hz), 3.31 (s, 3H), 4.09 (septet, 2H, J_{HH} = 6.84 Hz), 3.29 (s, 3H), 6.32-7.69 (m, 40H), 7.88 (d, 1H, J_{HP} = 9.28 Hz); ^{13}C NMR (C$_6$D$_6$): δ 22.6, 25.6, 28.8,

55.4, 113.1, 117.6, 121.2, 122.6, 123.7, 125.0, 125.2, 126.0, 129.4, 131.6, 132.0, 134.5 (d, J_{CP} = 9.76 Hz), 138.2, 140.6, 149.4, 150.4, 161.9, 165.7; ^{31}P NMR (C_6D_6): δ 24.63, Anal. Calcd for $C_{44}H_{44}NNiO_2P$: C, 74.59; H, 6.26; N, 1.98. Found: C, 74.01; H, 6.20; N, 1.65.

<u>Example XXVII</u>

[O-5-(NO₂)C₆H₃-o-C(H)=N-2,6-C₆H₃(i-Pr)₂]Nickel(phenyl)(PPh₃)

In a Schlenk flask was dissolved the Na salt of the compound of Example XXIV (0.56 g, 1.6 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at reflux for 1 hour. After this time, the reaction was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ~5 mL. Pentane (30 mL) was added to the vigorously stirred solution. A light-green solid precipitated from solution, and was isolated by cannula filtration to yield 0.84 g (89%) of a yellow-orange solid. ^{1}H NMR (C_6D_6): δ 0.96 (d, 6H, J_{HH} = 6.96 Hz), 1.22 (d, 6H, J_{HH} = 6.96 Hz), 3.89 (septet, 2H, J_{HH} = 6.96 Hz), 5.91-7.90 (m, 30H), 8.06 (d, 1H, J_{HP} = 2.92 Hz); ^{13}C NMR (C_6D_6): δ 22.2, 25.5, 28.7, 118.4, 121.4, 122.4, 122.6, 123.3, 125.2, 126.1, 128.0, 128.3, 129.9, 130.4, 130.9, 131.7, 134.2 (d, J_{CP} = 9.91 Hz), 137.5, 140.1, 149.0, 165.8, 170.5; ^{31}P NMR (C_6D_6): δ 25.51.

<u>Example XXVIII</u>

[O-3,5-Cl₂C₆H₂-o-C(H)=N-2,6-C₆H₃(i-Pr)₂]Nickel(phenyl)(PPh₃)

In a Schlenk flask was dissolved the Na salt of the compound of example XXV (0.66 g, 1.5 mmol) and bis(triphenylphosphine)nickel(phenyl)chloride (1.0 g, 1.4 mmol) in benzene (20 mL). The reaction was stirred at room temperature for 1 hour. After this time, the

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reaction was filtered by cannula filtration, and the
filtrate was concentrated in vacuo to ~5 mL. Pentane (30
mL) was added to the reaction. A yellow-orange solid
precipitated from solution, and was isolated by cannula

5   filtration to yield 0.91 g (74%) of a yellow-orange
solid. ^{1}H NMR (C_6D_6): δ 0.98 (d, 6H, J_{HH} = 6.80 Hz), 1.22
(d, 6H, J_{HH} = 6.80 Hz), 3.92 (septet, 2H, J_{HH} = 6.80 Hz),
6.25-7.67 (m, 30H); ^{13}C NMR (C_6D_6): δ 22.6, 25.5, 28.8,
117.4, 120.0, 122.8, 125.3, 126.2, 128.3, 128.6, 129.7,

10   130.5, 131.0, 131.5, 133.3, 133.8, 134.0, 134.4 (d, J_{CP} =
9.77 Hz), 137.4, 140.1, 149.4, 159.6, 165.2; ^{31}P NMR
(C_6D_6): δ 25.93. Anal. Calcd for $C_{43}H_{40}Cl_2NNiOP$: C, 69.29; H,
5.41; N, 1.88. Found: C, 69.87; H, 5.74; N, 1.63.

15   Example XXIX
                 p-Trifluoromethylsalicylaldehyde
           To a solution of p-trifluoromethylphenol (7.1g, 44
mmol) and 2,6-lutidine (1.9 g, 17.6 mmol) in toluene (80
mL) was slowly added $SnCl_4$ (1.2g, 4.4 mmol). The solution

20   was stirred at room temperature for 20 minutes.
Paraformaldehyde was added (3.2 g, 106 mmol) and the
reaction was stirred at 110°C for 12 hours. After cooling
to room temperature, the reaction mixture was poured into
water (250 mL), and adjusted to pH 1 with concentrated

25   HCl. The mixture was extracted with diethyl ether (500
mL), and the organic layer was washed twice with
saturated brine and dried over Na_2SO_4. The solvent was
removed by rotary evaporation to leave a yellow oil. The
oil was loaded onto a silica gel column and eluted with

30   6:1 hexane:ethyl acetate. The yield of product was 1.0 g
(12%). ^{1}H NMR(CDCl$_3$):δ 7.21-7.91 (m, 12H), 9.91 (s, 1H),
11.32 (s, 1H).

Example XXX

HO-5-(CF$_3$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$

To a methanol (10 mL) solution of 5-trifluoro-
methylsalicylaldehyde (0.7 g, 4.1 mmol) was added formic
5   acid (0.5 mL) and 2,6-diisopropylaniline (0.8 g, 4.5
mmol). The resulting mixture was stirred at room
temperature for 15 minutes. After this time, it was kept
at -80°C for 1 hour, yellow crystals precipitated from the
solution. The crystals were filtered, dried under vacuum
10   to yield 1.2 g (85%) of a yellow solid. ^{1}H NMR (C$_6$D$_6$):δ
1.04 (d, 12H), 2.85 (septet, 2H, J_{HH}=6.88 Hz), 6.85-7.25
(m,5H), 7.61 (s,1H), 13.82 (s,1H).

Example XXXI

[O-5-(CF$_3$)C$_6$H$_3$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$]Nickel(phenyl)(PPh$_3$)

15   In a Schlenk flask was dissolved the Na salt of
Example XXX (0.4 g, 0.6 mmol) and bis(triphenyl-
phoshine)nickel (phenyl)chloride 0.46g, 0.6 mmol) in
benzene (15 mL). The reaction was stirred at room
20   temperature for 1 hour. After this time, the reaction
was filtered by cannula filtration, and the filtrate was
concentrated in vacuo to ~2 mL. Pentane (20 mL) was
added to the vigorously stirred solution, which was then
cooled to -78°C. A yellow-orange solid precipitated from
25   solution, and was isolated by cannula filtration to yield
0.6g (65%) of a yellow-orange solid. ^{1}H NMR(C$_6$D$_6$):δ 0.95
(d, 6II, J_{HH}=6.84 Hz), 1.20 (d, 6H, J_{HH}=6.84 Hz), 3.95
(septet, 2H, J_{HH}=6.84 Hz), 6.32-7.81 (m, 40H, 31p NMR
(C$_6$D$_6$):δ 26.10.

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Example XXXII
HO-3,5-(NO$_2$)$_2$C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$
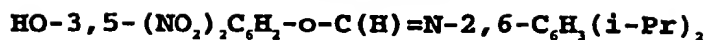
3,5-dinitrosalicylaldehyde was converted to the corresponding salicylaldimine by reaction with 2,6-diisopropylaniline according to the general procedure of Example XXIV. The yield of the 3,5-dinitrosalicylaldimine compound was 70%.

Example XXXIII
[O-3,5-(NO$_2$)$_2$C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$]Nickel(phenyl)(PPh$_3$)
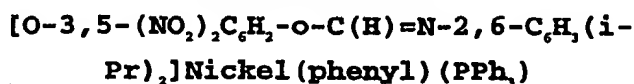
The product of Example XXXII was reacted with bis(triphenylphosphine)nickel (phenyl) chloride according to the general procedure of Example XXVII. The yield of the 3,5-dinitrosalicylaldimine nickel (II) complex was 58%.

Example XXXIV
General Procedure for Nitration of 3-R^1-Salicylaldehydes

To a solution of 5 mmol of the 3-R^1-salicylaldehyde in 10 ml of glacial acetic acid is added at room temperature 1 or 2 equivalents of concentrated HNO$_3$. After stirring for 40 minutes at room temperature, the mixture is poured into 100 ml of water. The yellow precipitate is collected by vacuum filtration, washed with water and dried in vacuo.

Using this procedure, the following 3-R^1-salicylaldehydes were nitrated (yield of nitration product in parentheses): 6-t-butylsalicylaldehyde (82%), 6-phenylsalicylaldehyde (71%), and 2-(9-anthracene)salicylaldehyde from Example XII (88% for mono-nitration at the 10-position of anthracene, 64% for di-nitration at the 10 position of the anthracene and *para*-position of the salicylaldehyde ring).

Example XXXV

HO-(3-t-Bu)(5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$

The nitrated product of t-butylsalicylaldehyde
prepared according to the general procedure of Example
XXXIV was converted to the imine by condensation with
2,6-diisopropylaniline using a procedure analogous to
Example III. The yield of the imine derivative was 63%.

Example XXXVI

[O-(3-t-Bu)(5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-
Pr)$_2$]Nickel(phenyl)(PPh$_3$)
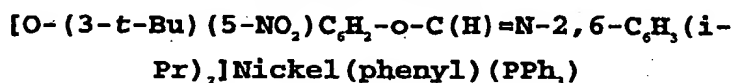
The Na salt of the product from Example XXXV was
reacted with bis(triphenylphosphine)nickel(phenyl)
chloride according to a procedure analogous to Example V.
The yield of the salicylaldimine nickel (II) complex was
40%.

Example XXXVII

HO-(3-Ph)(5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$
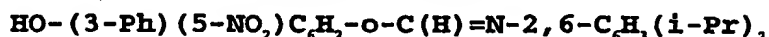
The nitrated product of 6-phenylsalicylaldehyde
prepared according to the general procedure of Example
XXXIV was converted to the corresponding imine by
condensation with 2,6-diisopropylaniline using a
procedure analogous to Example IV. The yield of the
imine derivative was 83%.

Example XXXVIII

[O-(3-Ph)(5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_3$(i-
Pr)$_2$]Nickel(phenyl)(PPh$_3$)
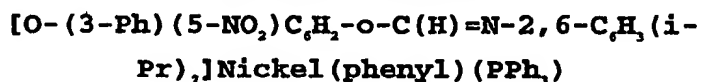
The Na salt of the product from Example XXXVII
was reacted with bis(triphenylphosphine)nickel(phenyl)
chloride according to a procedure analogous to Example

VI. The yield of the salicylaldimine nickel (II) complex
was 77%.

Example XXXVIX
OH-3-[9-(10-NO₂-Anthracene)](5-NO₂)C₆H₂-o-C(H)=N-2,6-C₆H₃(i-Pr)₂

The di-nitrated product of 2-(anthracene)
salicylaldehyde (see Example XII for synthesis of this
aldehyde), prepared according to the general procedure of
Example XXXIV, was converted to the corresponding imine
by condensation with 2,6-diisopropylaniline using a
procedure analogous to Example XIII. The yield of the
imine derivative was 66%.

Example XL
{O-3-[9-(10-NO₂-Anthracene)](5-NO₂)C₆H₂-o-C(H)=N-2,6-C₆H₃(i-Pr)₂}
Nickel(phenyl)(PPh₃)

The Na salt of the product from Example XXXVIX was
reacted with bis(triphenylphosphine)nickel(phenyl)
chloride according to a procedure analogous to Example
XIV. The yield of the salicylaldimine nickel (II)
complex was 72%.

Example XLI
HO-3-[9-(10-NO₂-Anthracene)]C₆H₃-o-C(H)=N-2,6-C₆H₃(i-Pr)₂

The mono-nitrated product of 2-(anthracene)
salicylaldehyde (see Example XII for synthesis of this
aldehyde), prepared according to the general procedure of
Example XXXII, was converted to the corresponding imine
by condensation with 2,6-diisopropylaniline using a
procedure analogous to Example IX. The yield of the
imine derivative was 70%.

<u>Example XLII</u>

**{O-3-[9-(10-NO$_2$-Anthracene)]C$_6$H$_3$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$}
Nickel(phenyl)(PPh$_3$)**

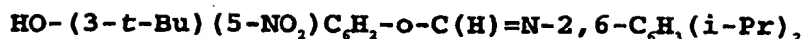The Na salt of the product from Example XLI was
reacted with bis(triphenylphosphine)nickel(phenyl)
chloride according to a procedure analogous to Example
XIV. The yield of the salicylaldimine nickel (II)
complex was 70%.

<u>Example XLIII</u>

HOC$_{10}$H$_6$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$

To a solution of 5.75 of 2-hydroxynaphthaldehyde and
7.6 mL of 2,6-diisopropylaniline in 100 mL of benzene was
added 0.32 g of p-toluenesulfonic acid. The mixture was
heated at reflux using a Dean-Stark trap for 16 hours.
After cooling to room temperature, the solvent is
evaporated on a rotary evaporator. Upon addition of 30
mL of methanol to the residue, an orange precipitate was
formed. The precipitate was filtered and dried in vacuo.
The yield of orange solid was 85%.

<u>Example XLIV</u>

[OC$_{10}$H$_6$-o-C(H)=N-2,6-C$_6$H$_3$(i-Pr)$_2$]Nickel(phenyl)(PPh$_3$)

The Na salt of the product of Example XLIII was
prepared by reaction of the product of Example XLIII (2.0
g) in 60 mL of THF with 0.30 g of NaH. The mixture was
stirred for 1 hour at room temperature. After filtration
of the reaction solution through a frit filter containing
Celite, the solvent was evaporated. The yield of Na salt
was 97%.

To a mixture of 0.49 g of the Na salt of the product
of Example XLIII and 0.96 g of
bis(triphenylphosphine)nickel(phenyl) chloride was added
at room temperature 30 mL of benzene. After stirring at
room temperature for 5 hours, themixture was filtered

(frit with Celite) and the volume of the dark red
solution was reduced in vacuo to ~3 mL. Pentane (30 mL)
was added and the mixture was cooled to -50 °C. An orange
precipitate was formed. The precipitate was filtered and
5   dried in vacuo. The yield of orange solid was 75%.

                         Example XLV
          Some of the above late transition metal
     salicylaldimine late transition metal chelates were used
10   in the catalytic polymerization of ethylene according to
     the following general procedure: The catalyst, in
     amounts indicated in the below table, was weighed and
     placed into a pressure container under an atmosphere of
     nitrogen. The pressure container was then evacuated and
15   backfilled with ethylene. 80 mL of dry toluene was then
     cannula transferred into the pressure container followed
     by addition of 5 mL of a toluene solution containing the
     phosphine sponge adjunct, bis(cyclooctadiene-
     nickel[Ni(COD)$_2$] or tris(pentafluorophenyl) boron
20   [(B(C$_6$F$_5$)$_3$]. The ethylene pressure was raised to that
     indicated in Table 1 below and maintained at the
     prescribed pressure. The indicated temperature was the
     initial temperature of the reactor. In all reactions
     (except those run at 0°C) the temperature was allowed to
25   rise due to the reaction exotherm. The reaction was run
     with stirring for forty minutes. The polymerization
     process was terminated and 500 mL of methanol was added
     to the toluene solution to precipitate the polyethylene
     product. The polyethylene was collected by filtering the
30   material through a glass frit filter. The number of
     branches of C$_1$ + C$_2$ + C$_3$ + C$_4$ and higher of the polymer was
     estimated using ^{13}C NMR analysis of the resultant polymer
     in hot 1,3,5-trichlorobenzene. Polymer molecular weight
     was determined by gel permeation chromatography in

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trichlorobenzene at 135°C and is relative to broad
polyethylene calibration standards.

Example XLVI
OH-3-(9-Anthracene)C_6H_3-o-C(H)=N-2,6-C_6H_2(i-Pr)$_2$(4-NO$_2$)

The 3-(anthracene) salicyladehyde was converted to
the corresponding imine by condensation with 2,6-
diisopropyl-4-nitroaniline using a procedure analogous to
Example XIII. The yield of the imine derivative was 81%.

Example XLVII
(O-3-(9-Anthracene)C_6H_3-o-C(H)=N-2,6-C_6H_2(i-Pr)$_2$(4-NO$_2$))
Nickel(phenyl)(PPh$_3$)

In a Schlenk flask was dissolved the Na salt of the
product of Example XLVI (1.44 g, 2.15 mmol) and
bis(triphenylphosphine)nickel(phenyl) chloride (1.45 g,
2.08 mmol) in benezene (25 mL). The reaction was stirred
at room temperature for 16 hours. After this time the
reaction was evaporated, the residue extracted with
methylene chloride (25 mL), filtered by cannula
filtration, and the filtrate was evaporated. The residue
was washed with pentane (25 ml) and dried in vacuum to
yield 1.00 g (52%) of an orange solid.

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Example XLVIII
OH-3-[9-(10-NO$_2$-Anthracene)](5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_2$(i-Pr)$_2$(4-NO$_2$)

The di-nitrated product of 3-(anthracene) salicyladehyde (see Example XII for synthesis of this aldehyde), prepared according to the general procedure of Example XXXIV, was converted to the corresponding imine by condensation with 2,6-diisopropyl-4-nitroaniline using a procedure analogous to Example XIII. The yield of the imine derivative was 50%.

Example XLVIX
(O-3-[9-(10-NO$_2$-Anthracene)](5-NO$_2$)C$_6$H$_2$-o-C(H)=N-2,6-C$_6$H$_2$(i-Pr)$_2$(4-NO$_2$))Nickel(phenyl)(PPh$_3$)

The Na salt of the product of Example XLVIII was reacted with bis(triphenylphosphine)nickel(phenyl) chloride according to a procedure analogous to Example XLVII. The yield of the salicylaldimine nickel (II) complex was 70%.

Polymerization of Ethylene

Table 1

Cat. Ex. No.	[Cat] mM	Adjuct equiv.	Temp C°	Press (psi)	Yield (g)	PDI[a]	Mw	Branches Total/ 1000
II	1.8	2[2]	25	80	2.0	1.54	4,000	45
II	1.8	2[2]	25	200	2.4	1.45	10,000	20
V	1.8	2[2]	25	80	8.0	2.25	26,000	55
VI	1.8	2[2]	25	80	20.0	2.28	23,300	40
V	0.9	2[2]	25	80	3.5	1.84	11,400	55
VI	0.9	2[2]	25	80	8.9	1.95	11,000	45
V	0.9	2[2]	0	80	3.1	3.10	6,600	25
VI	0.9	2[2]	0	80	3.9	2.45	108,000	10
V	0.9	2[2]	25	80	3.5	1.84	18,400	55
V	0.9	8[2]	25	80	4.8	2.34	43,200	40
V	0.9	1[2]	25	80	4.2	1.69	10,400	55
V	0.9	2[2]	25	80	3.3	2.55	11,000	45
XIV[b]	0.9	2[2]	25	80	7.0	3.85	37,700	30
XIV[b]	0.5	2[2]	25	80	0.8	2.30	56,700	5
XIV[b]	0.9	2[2]	25	80	7.0	6.84	49,500	35
XIV[b]	0.9	0.5[2]	25	80	5.0	3.63	42,500	20
XIV[b]	0.9	–	25	80	0.4	2.53	14,900	15
XV[b]	0.9	2[2]	25	80	7.4	6.43	54,000	0
XV[b]	0.9	2[2]	25	80	5.0	7.19	23,800	50
XXVI[b]	0.9	2[2]	25	80	1.0	1.68	7,300	39
II[b]	0.9	2[2]	25	80	2.0	1.54	4,000	
XXVII[b]	0.9	2[2]	25	80	8.0	18.0	143,000	32
XXVIII[b]	0.9	0.5[2]	25	80	1.5	3.28	22,500	9
XXVII[b]	0.5	1.0	25	80	3.0	18.0	366,000	12
XXXI	1.8	2[2]	25	80	0.9			
XXXI	0.9	2[2]	25	80	2.7			
XXXIII	1.8	2[2]	25	80	7.7			
XXXVI	0.9	2[2]	25	80	3.2			~25[c]
XXXVIII	0.9	2[2]	25	80	7.0			~13[c]
XL	0.9	2[2]	25	80	6.5			~20[c]
XL	0.9	2[2]	25	80	9.7			~55[c]
XLII	0.9	2[2]	25	80	4.0			~15[c]
XLII	0.9	2[2]	25	80	3.3			~5[c]
XLII	0.9	2[2]	25	80	7.0			~22[c]
XLIV	0.5	2[2]	50	80	2.3			
XLIV	0.9	2[2]	25	80	2.3			
XLIV	0.9	2[2]	25	80	0.4			

[a] PDI = Polydispersity index, Mw/Mn
[b] Polymerization run 15 minutes
[c] Estimated from peak melting temperature on DSC scan.
[1] Adjunct used was Ni(COD)$_2$
[2] Adjunct used was B(C$_6$F$_5$)$_3$

Example L

A series of polymerizations were carried out using nickel (II) salicylaldimine catalyst of the present invention, alone or, as part of a catalyst composition, in combination with a co-catalyst adjunct agent B(C$_6$F$_5$)$_3$,

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and/or a Lewis base. The procedures under which these polymerizations were conducted are outlined herein below and the specifics and results are given in the Tables which follow.

The salicylaldimine catalysts used are of compound I type wherein:

Catalyst "A": R^1 is 9-anthracenyl; R^2, X, R^3, and R^4 are each hydrogen; R^5 is 2,6-diisopropyl phenyl; R^6 is phenyl; L is triphenyl phosphine; A is oxygen and M is nickel.

Catalyst "B": R^1 is phenyl; R^2, X, R^3, and R^4 are each hydrogen; R^5 is 2,6-diisopropylphenyl; R^6 is phenyl; L is triphenyl phosphine; A is oxygen and M is nickel.

Catalyst "C": R^1 is 9-phenanthracenyl; R^2, X, R^3, and R^4 are each hydrogen; R^5 is 2,6-diisopropyl phenyl; R^6 is phenyl; L is triphenyl phosphine; A is oxygen and M is nickel.

Catalyst "D": R^1 is hydrogen; R^2, X, R^3, and R^4 are each hydrogen; R^5 is 2,6-diisopropylphenyl; R^6 is phenyl; L is triphenyl phosphine; A is oxygen and M is nickel.

Catalyst "E": R^1 is 9-phenanthracenyl; R^2, R^3 and R^4 are each hydrogen; X is nitro; R^5 is 2,6-diisopropylphenyl; R^6 is phenyl; L is triphenyl phosphine; A is oxygen and M is nickel.

Catalyst "F": R^1 is phenyl; R^2, R^3 and R^4 are each
                 hydrogen; X is nitro; R^5 is 2,6-
                 diisopropylphenyl; R^6 is phenyl; L is
                 triphenyl phosphine; A is oxygen and M is
5   nickel.

Catalyst "G": R^1 is 10-nitroanthracenyl; R^2, R^3 and R^4 are
                 each hydrogen; X is nitro; R^5 is 2,6-
                 diisopropylphenyl; R^6 is phenyl; L is
10   triphenyl phosphine; A is oxygen and M is
                 nickel.

Catalyst "H": R^1 is 10-nitroanthracenyl; R^2, R^3, R^4 and X
                 are each hydrogen; R^5 is 2,6-
15   diisopropylphenyl; R^6 is phenyl; L is
                 triphenyl phosphine; A is oxygen and M is
                 nickel.

Catalyst "I": R^1 is phenyl; R^2, R^3 and R^4 are each
20   hydrogen; X is nitro; R^5 is 2,6-
                 diisopropylphenyl; R^6 is phenyl; L is
                 triphenyl phosphine; A is oxygen and M is
                 nickel.

25 Catalyst "J": R^1 is 10-nitroanthracenyl; R^2, R^3 and R^4 are
                 each hydrogen; X is nitro; R^5 is 2,6-
                 diisopropylphenyl; R^6 is phenyl; L is
                 triphenyl phosphine; A is oxygen and M is
                 nickel.

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(1) Polymerization with catalyst composition containing
     catalyst of Compound I with $B(C_6F_5)_3$ as co-catalyst
     adjunct and diethyl ether as Lewis base additive.

The appropriate amount of Ni complex and co-catalyst
adjunct were weighed into a 6 oz glass pressure bottle
under an atmosphere of N_2. The solvent (generally 90 mL
dry toluene) was then cannula transferred into the
pressure bottle under a positive pressure of ethylene,
followed by the specified amount of diethyl ether. The
ethylene pressure was raised and maintained between 85
and 100 psig. When specified, temperature control was
accomplished by a water bath to control the exotherm.
Stirring of the reaction mixture was maintained by a
magnetic stirrer and stir bar. After completion of the
polymerization reaction, methanol (1000 mL) and 1N
hydrochloric acid (50 mL) was added to the toluene
solution to precipitate the polymer and remove catalyst
residue. The polyethylene product was collected by
filtration through a glass frit, washed with methanol
(100 mL) and dried under vacuum.

(2)   Polymerization with catalyst of Compound I without
       co-catalyst adjunct or Lewis base additive.

The appropriate amount of Ni complex was weighed
into either a 6 or 12 oz. glass pressure bottle under an
atmosphere of N_2. The solvent (90 mL) was then cannula
transferred into the pressure bottle under a positive
pressure of ethylene. The ethylene pressure was raised
and maintained between 85 and 100 psig. When specified,
temperature control was accomplished by a water bath to
control the exotherm. Stirring of the polymerization
mixture was maintained by a magnetic stirrer and stir
bar. In cases where the viscosity of the polymerization
mixture increased to the point where ethylene consumption
slowed significantly, the pressure was released and
additional amounts of solvent were added. Subsequently,

the mixture was re-pressurized with ethylene. After
completion of the polymerization reaction, methanol (1000
mL) and 1N hydrochloric acid (50 mL) was added to the
toluene solution to precipitate the polymer and remove

5   catalyst residue. The polyethylene product was collected
by filtration through a glass frit, washed with methanol
(100 mL) and dried under vacuum.

(3)   Polymerization with catalyst composition composed of

10   catalyst of Compound I with different Lewis base
additives.

The appropriate amount of Ni complex was weighed
into either a 6 or 12 oz. glass pressure bottle under an

15   atmosphere of N_2. The solvent (90 mL) was then cannula
transferred into the pressure bottle under a positive
pressure of ethylene, followed by the specified amount of
additive. The ethylene pressure was raised and
maintained between 85 and 100 psig. When specified,

20   temperature control was accomplished by a water bath.
Stirring of the polymerization mixture was maintained by
a magnetic stirrer and stir bar. In cases where the
viscosity of the polymerization mixture increased to the
point where ethylene consumption slowed significantly,

25   the pressure was released and additional amounts of
solvent were added. Subsequently, the mixture was re-
pressurized with ethylene. After completion of the
polymerization reaction, methanol (1000 mL) and 1N
hydrochloric acid (50 mL) was added to the toluene

30   solution to precipitate the polymer and remove catalyst
residue. The polyethylene product was collected by
filtration through a glass frit, washed with methanol
(100 mL) and dried under vacuum.

(4)   Polymerizations carried out at elevated ethylene
       pressure.

       A 1.5 liter Parr stainless steel reactor was charged
with the appropriate amount of Ni complex, the specified
volume of benzene, and diethyl ether in a dry box under
an atmosphere of N_2. The reactor was assembled, removed
from the dry box, and pressurized with ethylene (500 psig
unless specified otherwise). The ethylene pressure was
maintained between 490 and 500 psig unless specified
otherwise. No temperature control was provided.
Stirring of the reaction mixture was maintained by a
magnetic stirrer and stir bar. After completion of the
polymerization reaction, methanol (1000 mL) and 1N
hydrochloric acid (50 mL) was added to the benzene
solution to precipitate the polymer and remove catalyst
residue. The polyethylene product was collected by
filtration through a glass frit, washed with methanol
(100 mL) and dried under vacuum.

(5)   Copolymerizations with functional cyclic olefins.

       The appropriate amount of Ni complex was weighed
into a 12 oz. Fisher Porter pressure bottle under an
atmosphere of argon in a dry box. A mechanical stirring
assembly and thermocouple was attached, and the apparatus
was removed from the dry box. The pressure bottle was
evacuated, then back-filled with ethylene. Dry toluene
(100 mL) was cannula transferred into a nitrogen-flushed
stainless steel container fitted with a two-way valve.
The container was then pressurized to 50 psig (unless
specified otherwise) with ethylene. Dry diethyl ether
(10 or 20 mL) was cannula transferred into another
nitrogen-flushed stainless steel container fitted with
two-way valve and the container was pressurized to 50

psig with ethylene. Into another stainless steel
container fitted with two-way valve, a solution of
functionalized monomer in a small volume of dry toluene
was cannula transferred and the container was pressurized

5   with ethylene to 50 psig. In rapid sequential fashion,
the toluene, ether and solution of functionalized
monomer, all under positive ethylene pressure (50 psig),
were blown into the Fisher Porter bottle. A water bath
(40-45°C) was used to gently warm contents of the bottle.

10   The bottle was pressurized to 50 psig with ethylene and
maintained at 50 psig over the course of the
copolymerization reaction. The reaction typically
exothermed to a temperature between 45-55 °C. When the
uptake of ethylene became negligible, the ethylene

15   pressure was released and the contents of the bottle were
poured into 1 liter of methanol or acetone. The
precipitated polymer was collected by vacuum filtration,
re-suspended in a large volume of methanol, filtered,
washed with fresh methanol and dried under vacuum.

Table 2. Polymerization of Ethylene with Catalyst Composition Containing Cocatalyst Adjunct and Lewis Base Additive.[a]

Sample	Vol. of Et₂O (mL)	Catalyst	Temperature control	Catalyst Productivity (kg PE /mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
1	0.1	A	no	84.6	5.5	35,600	3.7	120	37
2	0.5	A	no	84.6	5.5	32,500	4.2	119	35
3	1	A	no	92.3	6.0	31,900	4.8	121	42
4	2	A	no	107.7	7.0	32,600	5.3	122	47
5	5	A	no	104.6	6.8	31,000	5.9	122	51
6	10	A	no	130.8	8.5	33,200	5.1	122	41
7	20	A	no	103.1	6.7	33,000	6.0	125	40
8	90[e]	A	no	69.2	4.5	57,000	2.8	123	32
9	5[f]	A	no	57.5	3.9	78,200	2.0	129	6
10	5	A	yes	189.2	12.3	91,300	3.3	126	22
11	10[d]	A	yes	424.6	27.6	172,000	2.7	126	13
12	90[c,d]	A	yes	144.6	9.4	106,000	2.4	129	28
13	90[f]	B	yes	103	6.8	15,900	2.2	85	

[a] All polymerizations reactions were carried out with 55 mg of Ni complex and 2 eq. of co-catalyst adjunct, B(C₆F₅)₃ in toluene (90 mL) at 80-90 psig of ethylene. [b] Total number of C₁+C₂+C₃+C₄ and higher branches per 1000 carbons. [c] Diethyl ether used as only solvent. [d] More solvent added during the reaction. [e] THF used as only solvent. [f] Ethyl vinyl ether used.

Table 2 essentially shows the use of Lewis base
additive as part of catalyst compositions comprising a
co-catalyst adjunct, $B(C_6F_5)_3$, with nickel (II)
salicylaldimine catalyst. In total, the data show that
catalyst productivity and polymer yield increase with
increasing amount of diethyl ether. In entries where no
temperature control was used, there does not appear to be
a significant influence of the ether on the branching of
the polyethylene produced (except ethyl vinyl ether). In
instances where the polymerization reaction temperature
was controlled, the data shows that catalyst productivity
and polymer yield is further enhanced. Significantly,
polymer molecular weight is increased and the molecular
weight distribution (PDI) narrows when the temperature is
controlled. Samples 8, 12 and 13 of Table 2 reveal that
the catalyst is active when ether is present as solvent.
Taken together, data in the table also indicate that the
nickel salicylaldimine catalyst performs well with small
or even large amounts of a Lewis base compound, such as
ether.

Table 3. Polymerization of Ethylene Without Adjunct or Lewis Base Additive[a]

Sample	Entry	Catalyst Productivity (kg PE/mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
14[c]	A	842	55.1	77,300	6.2	120.8	23
15[c]	A	1038	66.7	70,000	5.5	120.1	25
16	E	575	37.4	354,000	2.8	136.7	5
17	F	246	16.1	247,000	3.2	131.1	10
18	H	107	6.9	177,000	2.4	135.4	5
19	G	776	50.7	238,000	3.6	132.7	8
20	I	938	60.5	236,000	2.2	135.5	5
21	J	432	28.2	252,000	2.7	134.0	6
22	B	212	14.1	207,000	2.2	132.9	10
23	C	617	40.4	207,000	2.4	129.5	8

[a] All polymerizations reactions were carried out with 65 μmol of Ni complex in toluene (90 mL initially) at 80-90 psig of ethylene with temperature control.

[b] Total number of $C_1+C_2+C_3+C_4$ and higher branches per 1000 carbons. [c] More solvent added during the reaction.

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Table 3 illustrates that nickel (II) salicylaldimine
family of catalysts are active polymerization catalysts
without any co-catalyst adjunct or Lewis base present.
5   This demonstrates that this family of catalyst are true
single-component polymerization catalysts.

Table 4. Polymerization of Ethylene with Catalyst "A" and Diethyl Ether as Additive.[a]

Sample	Catalyst loading	Vol. of Et$_2$O (mL)	Catalyst Productivity (kg PE/mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
24	55 mg	10[c]	781.8	43.0	165,000	2.2	127	34
25	55 mg	10[c]	923.6	50.8	90,600	7.0	122	25
26	25 mg	5[c,d]	1220	30.5	62,800	5.5	120	28
27	10 mg	5[c,d]	430.0	4.3	193,000	2.0	132	10

[a] All polymerizations reactions were carried out in toluene (90 mL) at 80-90 psig of ethylene with temperature control. [b] Total number of C$_1$+C$_2$+C$_3$+C$_4$ and higher branches per 1000 carbons. [c] More solvent added during the reaction. [d] Only 50 mL of toluene used at the beginning of the reaction.

The significance of Table 4 is that it reveals that
the subject catalyst is very active in the presence of an
oxygenated Lewis base, such as ether. In comparison to
Table 3 (catalyst A, samples 14 and 15), the catalyst
productivity is shown to be similar. The data for
catalyst "A" in Table 4, as compared to catalyst "A" in
Table 3, show the benefit of Lewis base to the molecular
weight of the polyethylene product. For catalyst A,
polyethylene of higher molecular weight is generally
produced when the catalyst composition is comprised of
nickel (II) salicylaldimine catalyst and Lewis base.

Table 5. Polymerization of Ethylene with Catalyst A and Lewis Base Additives.[a]

Sample	Additive	Additive Amount	Catalyst Productivity (kg PE/mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
28	THF[c]	10 mL	467.3	25.7	270,000	2.4	133	5
29	1,4-Dioxane	10 mL	170.9	9.4	197,000	2.2	137	3
30	Dimethoxyethane[c]	10 mL	1289	70.9	270,000	2.4	136	3
31	Diglyme	10 mL	114.5	6.3	189,000	2.1	136	2
32	Triglyme[c]	10 mL	663.6	36.5	218,000	2.2	134	4
33	Tetraglyme[c]	10 mL	461.8	25.4	179,000	2.4	131	5
34	Anisole	10 mL	45.5	2.5	184,000	2.6	139	4
35	n-Butyl Ether	15 mL	58.2	3.2	184,000	2.3	135	4

[a] All polymerizations reactions were carried out with 55 mg of catalyst in toluene (90 mL) at 80-90 psig of ethylene with temperature control. [b] Total number of $C_1+C_2+C_3+C_4$ and higher branches per 1000 carbons. [c] More toluene added during the reaction.

Table 5 shows that other members of the ether family also are effective Lewis base additives for the polymerization of ethylene when used with the subject

5   catalyst. Dimethoxyethane appears to be most effective under the conditions used, as noted by the highest catalyst productivity and yield of PE. It should be noted that with temperature control, the catalyst/ether system produces highly linear polyethylene. The polymer

10   produced is essentially high density polyethylene having a low amount of branching and high melting point. Note also that cyclic ethers as well as linear polyethers are effective additives.

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Table 6. Polymerization of Ethylene with Catalyst "A" and Various Lewis Base Additives. [a]

Sample	Additive	Amount Additive	Catalyst Productivity (kg PE/mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
36	Acetone	10 mL	183.6	10.1	131,000	3.7	128	13
37	Ethylacetate	10 mL	121.8	6.7	188,000	2.0	138	
38	Ethanol	10 mL	12.7	0.7	46,600	3.0	129	17
39	Water	0.1 mL	63.6	3.5	90,100	2.0	130	4
40	Nitromethane	5 mL	52.7	2.9	140,000	2.4	133	5
41	N,N-Dimethylformamide	10 mL	63.6	3.5	140,000	2.4	133	5
42	Phenol	10 g	112.7	6.2	202,000	3.3	134	9
43	Triethylamine	10 mL	5.5	0.3	28,200	2.6	129	22

[a] All polymerizations reactions were carried out with 55 mg of catalyst in toluene (90 mL) at 80-90 psig of ethylene with temperature control. [b] Total number of $C_1+C_2+C_3+C_4$ and higher branches per 1000 carbons.

Table 6 demonstrates that the subject catalyst is active in the presence of other Lewis base compounds. Notably, the catalyst remains active and produces high molecular PE even in the presence of water. Ziegler-Natta, metallocene catalysts and cationic nickel single site catalysts are generally not known to tolerate water.

Table 7. Polymerization of Ethylene with Various Ni (II) Salicylaldimine Catalysts.[a]

Sample	Catalyst	Catalyst [mM]	Additive	Additive Amount	Catalyst Productivity (kg PE/mol Ni)	Yield PE (g)	M_w	PDI	T_m (°C)	Total Branches[b]
44	I	0.71	Et₂O	10 mL	720.0	46.8	197,000	3.5	134	5
45	I	0.71	DME	10 mL	224.6	14.6[c]	27,600	7.0	118	42
46	I	0.71	DME	10 mL	695.4	45.2	208,000	2.3	133	8
47	D	0.94	Et₂O	10 mL	14.5	0.8	11,400	1.8	95	42[d]
48	B	0.81	Et₂O	10 mL	85.5	8.2	68,000	4.7	120	26
49	F	0.82	Et₂O	10 mL	265.5	14.6	161,000	6.8	128	18
50	F[e]	0.65	Et₂O[c]	10 mL	469.1	25.8	72,300	5.7	119	19
51	C	0.71	Et₂O[c]	10 mL	472.7	26.0	257,000	2.4	131	5
52	C	0.71	DME[e]	5 mL	420.0	23.1	85,000	3.2	123	16
53	G[e]	0.60	Et₂O	5 mL	473.7	18.2	315,000	3.6	135.5	6
54	E[e]	0.73	Et₂o	10 mL	388.4	25.4	194,000	5.9	129.1	12

[a] All polymerization reactions were carried out in toluene (90 mL) at 80-90 psig of ethylene with temperature control. [b] Total number of $C_1+C_2+C_3+C_4$ and higher branches per 1000 carbons. [c] More toluene added during the reaction. [d] Olefinic species detected by NMR. [e] Reaction at 45°C.

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The data in the above Table 7 indicate that the subject catalysts are active catalysts for the polymerization of ethylene in the presence of Lewis base.

Table 8. Copolymerization of Ethylene and Functionalized Cyclic Olefins with Catalyst A and Diethyl Ether Additive.

Sample	Comonomer	Amount of Comonomer	Catalyst loading	Yield PE (g)	M_w	% Incorporation
48	5-NAc[c]	2 mL	100 mg	6.0		3.8 wt %
49	5-NAlc[d]	2 g	55 mg	1.0	17,200	22.8 wt %

[a] Polymerization was carried out with 55 mg Catalyst A and 20 ml diethyl ether in toluene (100 mL) at 50 psig of ethylene at 40°C.
[b] Polymerizationwas carried out with 55 mg Catalyst A and 10 ml diethyl ether in toluene (90 mL) at 40 psig of ethylene at room temperature.
[c] 5-NAc is 5-norbornen-2-yl acetate.
[d] 5-NAlc is 5-norbornen-2-ol.

The data in this Table 8 reveal that the subject catalyst can also copolymerize a polar olefinic monomer, such as functionalized norbornene.

Table 9. Comparative Ethylene Polymerizations at Elevated Pressure Between Present Catalyst and Nickel Based Catalyst, SHOP.[a,b]

Sample	Catalyst	Catalyst Concentration (mM)	Yield PE (g)	TON[c] (kg PE/mol cat*hr)	Catalyst Productivity (kg PE/mol Ni)	M_w	PDI	T_m (°C)	Total Branches
50	A	0.516[c]	60	930	546	132,000	18	130.1	19
51	A	0.129	77	1200	698	65,000	9.4	125.0	28
52	A	0.064	64	660	1156	73,800	6.4	122.6	28
53	A	0.029	61.0	350	2440	324,000	2.3	132.8	11
54	A	0.129	103		805[d]	85,000	9.8	124.1	24
55	A	0.129	153	402	1187[d]	190,000	11.7	127.0	15
56	A	0.033	78[f]	1178	2356[d]	347,000	3.0	136.1	5
57	SHOP	0.129	4	15.5	44	2,000	1.4	broad ~112	17
58	SHOP	0.129	11.1		86[d]	2,600	1.5	120.7	12[g]

[a] Polymerization reactions were carried out in a steel bomb with 1000 mL benzene and 100 mL Et_2O at 500 psig of ethylene without temperature control. [b] SHOP is a commercially available catalyst (see U.S. 4,716,205 for details of catalyst). [c] TON is turn over number which is measure of catalyst activity as a rate per hour. [d] No ether additive used in the polymerization reaction. [e] Reaction run with temperature control. [f] Ethylene pressure was 350 psig. [g] Some olefinic species detected.

Table 9 reveals that catalyst activity is generally
enhanced at higher ethylene pressure. The Table also
compares the activity of a subject catalyst with the SHOP
catalyst. The activity of the subject catalyst is
5   significantly higher (as much as 10^2 times greater) and
the polymer produced has lower branching and higher
molecular weight than observed with polymerizations using
the SHOP catalyst, with or without Lewis base additive.
Table 9 further indicates that polyethylene yield was
10   highest without the Lewis base present.

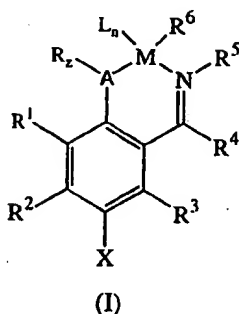   Example LI
The appropriate amount of Na salt of the product of
Example XIII and bis(triphenylphosphine)nickel(phenyl)
15   chloride were weighed into a 12 oz. Fisher Porter
pressure bottle under an atmosphere of N_2 in a dry box.
The solvent (90 mL of toluene) was then cannula
transferred into the pressure bottle under a positive
pressure of ethylene. The ethylene pressure was raised
20   and maintained between 85 and 100 psig. Temperature
control was accomplished by a water bath. Stirring of
the reaction mixture was maintained by a magnetic stirrer
and a stir bar. When the viscosity of the reaction
mixture increased to the point where ethylene consumption
25   slowed significantly, the pressure was released and
additional amounts of solvent were added. Subsequently,
the mixture was repressurized with ethylene. After
completion of the polymerization reaction, methanol (1000
mL) and 1 N hydrochloric acid (50 mL) was added to the
30   toluene solution to precipitate the polymer. The
polyethylene was collected by filtration through a glass
frit, washed with methanol (100 mL) and dried in vacuum.
The yield of polyethylene was 38.3 g. Catalyst
productivity corresponded to 578 kg PE/mol Ni. The
35   weight average molecular weight and polydispersity of the

polymer was 348,000 and 2.2, respectively. The peak
melting point was 136.5°C as determined by DSC.

The results of this polymerization demonstrate that
the catalyst of the present invention can be prepared *in
situ* by mixing compound V and a source of nickel atom
$\{R^6(L)_2MY\}$.

IN THE CLAIMS:

    1.   A compound represented by the formula

$$
\begin{array}{c}
L_n \quad R^6 \\
R_z\!-\!A\!-\!M\!-\!N\!-\!R^5 \\
R^1 \quad\quad\quad\quad\quad R^4 \\
R^2 \quad\quad\quad R^3 \\
X
\end{array}
$$

(I)

wherein

    R represents a C_1-C_{11} alkyl; aryl; or substituted aryl group and z is 0 when A is oxygen or sulfur and z is 1 when A is nitrogen;

    R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl; substituted aryl wherein the substitution group is selected from C_1-C_4 alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; siloxyl ($-OSiA_3$ where A is selected from phenyl or C_1-C_4 alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group ($-(BO)_zR^7$, wherein each B independently is selected from a C_1-C_4 alkylene or an arylene group, O represents oxygen, R^7 represents a C_1-C_{11} hydrocarbyl group and z is an integer of 1 to 4);

    R^2 represents hydrogen atom, aryl, substituted aryl, C_1-C_{11} alkyl, halogen atom or R^1 and R^2, together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

    R^3 represents hydrogen;

R^4 represents hydrogen atom; a C$_1$-C$_{11}$ alkyl; an aryl; substituted aryl group; or R^3 and R^4, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R^5 represents a C$_1$-C$_{11}$ alkyl; C$_5$-C$_8$ cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C$_1$-C$_4$ alkyl, the para position (with respect to the N-R^5 bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C$_1$-C$_4$ alkyl, sulfonate or fused or unfused aryl group; a hydrocarbyl terminated oxyalkylene group (-(BO)$_x$R^7); or R^1 and R^5 together form an oxyhydrocarbylene containing chain (-(BO)$_m$B- wherein each B is independently selected from a C$_1$-C$_4$ alkylene group or an arylene group and m is an integer of 1-4);

n represents an integer of 0 or 1;

R^6 represents, when n is 1, an unsubstituted or substituted aromatic group; a C$_1$-C$_{11}$ alkyl; a hydrogen atom or halogen atom or, when n is 0, R^6 represents an allyl group or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri(C$_1$-C$_6$ alkyl) phosphine tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, triphenoxyphosphine, trialkylamine, C$_2$-C$_{20}$ alkene, substituted C$_2$-C$_5$ alkene, C$_1$-C$_4$ alkoxy, pyridine, di(C$_1$-C$_3$ alkyl) ether, tetrahydrofuran, or a nitrile;

X represents a hydrogen atom or an electron withdrawing group selected from NO$_2$, halo, sulfonate (SO$_3^-$), sulfonyl ester (SO$_2$R), carboxyl (COO$^-$), a perfluoroalkyl, or a carboxylic ester group;

M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state; and

A represents oxygen, nitrogen or sulfur.

2. The compound of Claim 1 wherein R^1 is selected from aryl, substituted aryl or C_3-C_6 alkyl group.

3. The compound of Claim 1 wherein R^5 is selected from aryl or substituted aryl, alkyl or cycloalkyl.

4. The compound of Claim 2 wherein R^5 is selected from aryl or substituted aryl.

5. The compound of Claim 2 wherein R^5 is selected from alkyl or cycloalkyl.

6. The compound of Claim 1 wherein X is selected from nitro group, perfluoroalkyl group, sulfonate group, or halo atom.

7. The compound of Claim 1, 2, 3, 4, 5, or 6 wherein M is nickel atom or palladium atom.

8. The compound of Claim 1 wherein R^1 is selected from t-butyl, anthracenyl or phenanthracenyl.

9. The compound of Claim 2 or 8 wherein R^5 is 2,6-di(C_1-C_4 alkyl) phenyl group.

10. The compound of Claim 9 wherein R^5 is 2,6-di(isopropyl) phenyl.

11.   The compound of Claim 1 wherein X is a halogen atom.

12.   The compound of Claim 1 wherein R^1 is selected from a hydrocarbyl terminated oxyalkylene group represented by the formula $-(BO)_zR^7$ wherein B is a C_1-C_4 alkylene, O is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-4.

13.   The compound of Claim 1 wherein R^5 is selected from an aryl group substituted with a hydrocarbyl terminated oxyalkylene group represented by the formula $-(BO)_zR^7$ wherein B is a C_1-C_4 alkylene, O is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-4.

14.   The compound of Claim 1 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is anthracenyl.

15.   The compound of Claim 1 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenanthracenyl.

16.   The compound of Claim 1 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenyl.

17.   The compound of Claim 1 wherein R^1 and R^5 together represent a polyoxyhydrocarbylene group.

18.   The compound of Claim 14, 15 or 16 wherein R^5 is a 2,6-di(C_1-C_4 alkyl)-4-nitrophenyl group.

19.   The compound of Claim 14, 15, or 16 wherein X is selected from nitro group.

20. The compound of Claim 17 wherein X is selected from nitro group.

21. The compound of Claim 1, 12, 13, 14, 15, 16, or 17 wherein M is nickel atom or palladium atom.

22. The compound of Claim 1 wherein
    R^1 is anthracenyl;
    R^2, R^3, R^4 and X are each hydrogen;
    R^5 is 2,6-di(isopropyl) phenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium; and
    A is oxygen.

23. The compound of Claim 1 wherein
    R^1 is phenanthracenyl;
    R^2, R^3, R^4 and X are each hydrogen;
    R^5 is 2,6-di(isopropyl) phenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium; and
    A is oxygen.

24. The compound of Claim 1 wherein
    R^1 is phenyl;
    R^2, R^3, R^4 and X are each hydrogen;
    R^5 is 2,6-di(isopropyl) phenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium; and
    A is oxygen.

25. The compound of Claim 1 wherein
     R^1 is anthracenyl;
     R^2, R^3, R^4 and X are each hydrogen;
     R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium; and
     A is oxygen.

26. The compound of Claim 1 wherein
     R^1 is 10-nitroanthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is nitro.

27. The compound of Claim 1 wherein
     R^1 is phenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
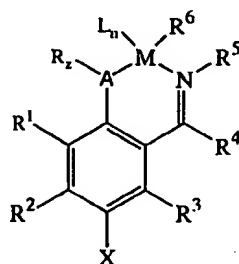   M is selected from nickel or palladium;
     A is oxygen; and
     X is nitro.

28. The compound of Claim 1 wherein

R^1 is 10-nitroanthracenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl)-4-nitro phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

29. The compound of Claim 1 wherein

R^1 is phenanthracenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl) phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

30. The compound of Claim 1 wherein

R^1 is 10-nitroanthracenyl;

R^2, R^3, R^4 and X are each hydrogen;

R^5 is 2,6-di(isopropyl) phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium; and

A is oxygen.

31. The compound of Claim 1 wherein
     R^1 is terphenyl;
     R^2, R^3, R^4 and X are each hydrogen;
     R^5 is 2,6-di(isopropyl)-4-nitro phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium; and
     A is oxygen.

32. The compound of Claim 1 wherein
     R^1 is anthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl)-4-nitro phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is nitro.

33. The compound of Claim 1 wherein
     R^1 is anthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is nitro.

34. The compound of Claim 1 wherein

R^1 is 10-nitroanthracenyl;

R^2, R^3, R^4 and X are each hydrogen;

R^5 is 2,6-di(isopropyl)-4-nitro phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium; and

A is oxygen.

35. The compound of Claim 1 wherein

R^1 is phenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl)-4-nitro phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

36. The compound of Claim 1 wherein

R^1 is terphenyl;

R^2, R^3, R^4 and X are each hydrogen;

R^5 is 2,6-di(isopropyl) phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium; and

A is oxygen.

37. A process of forming transition metal salicylaldimine complexes having the formula

(I)

wherein

R represents a C_1-C_{11} alkyl; aryl; or substituted aryl group and z is 0 when A is oxygen or sulfur and z is 1 when A is nitrogen;

R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl; substituted aryl wherein the substitution group is selected from C_1-C_4 alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; or siloxyl (-OSiA$_3$ where A is selected from phenyl or C_1-C_4 alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group -(BO)$_z$R^7, wherein each B independently is selected from a C_1-C_4 alkylene or an arylene group, O represents oxygen, R^7 represents a C_1-C_{11} hydrocarbyl group and z is an integer of 1 to 4;

R^2 represents hydrogen atom, aryl, substituted aryl, C_1-C_{11} alkyl, halogen atom or R^1 and R^2, together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R^3 represents hydrogen;

R^4 represents hydrogen atom, a C_1-C_{11} alkyl; an aryl; substituted aryl group; or R^3 or R^4, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R^5 represents a C_1-C_{11} alkyl; cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C_1-C_4 alkyl, the para position (with respect to the N-R^5 bond) substituted

5 with a hydrogen, nitro, trifluoromethyl, halogen, methoxy or C_1-C_4 alkyl or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group ($-(BO)_z R^7$); or R^1 and R^5 together form an oxyhydrocarbylene chain, $-(BO)_m B-$, wherein each B is independently selected from

10 C_1-C_4 alkylene group or an arylene group and m is an integer of 1-4;

n represents an integer of 0 or 1;

R^6 represents, when n is 1, an unsubstituted or substituted aromatic group; a C_1-C_{11} alkyl; a hydrogen atom

15 or halogen atom or when, n is 0, R^6 represents an allyl group or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri(C_1-C_6 alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine,

20 dialkylphenylphosphine, triphenoxyphosphine, trialkylamine, C_2-C_{20} alkene, substituted C_2-C_4 alkene, C_1-C_4 alkoxy, pyridine, di(C_1-C_3 alkyl)ether, tetrahydrofuran, or a nitrile;

X represents a hydrogen atom or an electron

25 withdrawing group selected from NO_2, halo, sulfonate (SO_3^-), sulfonyl ester ($SO_2 R$), carboxyl (COO^-), a perfluoroalkyl, or a carboxylic ester group;

M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe,

30 Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state; and

A represents oxygen, nitrogen or sulfur; comprising reacting an amine of the formula, $R^5 NH_2$ with a compound (II) of the formula

$$\begin{array}{c}
R_z-A \\
R^1 \quad\quad \overset{O}{\underset{}{\parallel}}\!\!-R^4 \\
R^2 \quad\quad R^3 \\
X
\end{array}$$

(II)
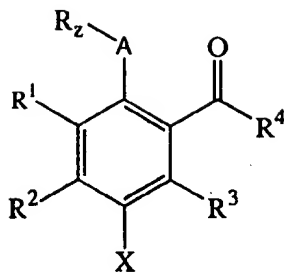
wherein each R^1, R^2, R^3, R^4, R^5, X and A are as defined
above to provide a bidentate ligand and

R of formula II independently represents hydrogen
atom, C_1-C_{11} alkyl; aryl; or substituted aryl, provided
that R represents at least one hydrogen atom, and z is 1
when A is oxygen or sulfur, or z is 2 when A is nitrogen;

deprotonating said ligand, and contacting the
deprotonated product with a transition metal compound
having the formula $R^6(L)_2MY$ wherein each R^6, L, Y and M are
as defined above.

38. The process of Claim 37 wherein

a) the amine and compound (II) are reacted at a temperature of from 15 to 80°C, for a period of from about 1 to 20 hours in an organic inert solvent;
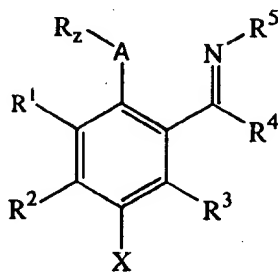
b)   the ligand is deprotonated by contacting said ligand with a deprotonating agent selected from alkali metal hydride, alkyl lithium or lithium dialkylamine, at a temperature of from about 0°C to about 30°C in an inert solvent; and

c)   the transition metal compound and deprotonated product are contacted in an inert solvent at a temperature of from about 10 to 90°C for a period of 1 to 15 hours.

39. The process of Claim 38 wherein step (a) is carried out at 15 to 25°C in a medium selected from C_1-C_3 alkanol, benzene or toluene for a period of 10 to 12 hours; step (b) is carried out at 0 to 10°C with sodium hydride as the agent in a medium selected from tetrahydrofuran, dialkylether, C_5-C_{10} hydrocarbon, dioxane, for a period of 5 to 30 minutes; and step (c) is carried out at 10 to 30°C in a medium of tetrahydrofuran, C_5-C_{10} hydrocarbon, or dialkyl ether, for a period of 10 to 15 hours.

40. A compound represented by the formula

$$R_z-A \qquad N-R^5$$

(IV)

wherein

R independently represents hydrogen atom; C_1-C_{11} alkyl; aryl; or substituted aryl, provided that R represents at least one hydrogen atom, and z is 1 when A is oxygen or sulfur or z is 2 when A is nitrogen;

R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl; substituted aryl wherein the substitution group is selected from C_1-C_4 alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; siloxyl ($-OSiA_3$ where A is selected from phenyl or C_1-C_4 alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group ($-(BO)_zR^7$ wherein each B independently is selected from a C_1-C_4 alkylene or an arylene group, O represents oxygen, R^7 represents a C_1-C_{11} hydrocarbyl group and z is an integer of 1 to 4);

R^2 represents hydrogen atom, aryl, substituted aryl, C_1-C_{11} alkyl, halogen atom or R^1 and R^2, together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R^3 represents hydrogen;

R^4 represents hydrogen atom, a C_1-C_{10} alkyl; an aryl; substituted aryl group; or R^3 or R^4, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocylic ring;

R^5 represents a C_1-C_{11} alkyl; C_5-C_8 cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C_1-C_4 alkyl, the para position (with respect to the N-R^5 bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C_1-C_4 alkyl, sulfonate or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group ($-(BO)_2R^7$); or R^1 and R^5 together form an oxyhydrocarbylene chain, $-(BO)_mB-$ wherein each B is independently selected from a C_1-C_4 alkylene group or an arylene group and m is an integer of 1-4;

X represents any electron withdrawing group selected from NO_2, halo, sulfonate (SO_3^-), sulfonyl ester (SO_2R), carboxyl (COO^-), a perfluoroalkyl, a carboxylic ester or a hydrogen atom; and

A represents oxygen, nitrogen or sulfur.

41. The compound of Claim 40 wherein R^1 is selected from aryl, substituted aryl or C_1-C_6 alkyl group.

42. The compound of Claim 40 wherein R^5 is selected from aryl or substituted aryl, alkyl or cycloalkyl.

43. The compound of Claim 41 wherein R^5 is selected from aryl or substituted aryl.

44. The compound of Claim 41 wherein R^5 is selected from alkyl or cycloalkyl.

45.   The compound of Claim 40 wherein X is selected
from nitro group, perfluoroalkyl group, sulfonate group,
or halo atom.

5   46.   The compound of Claim 40 wherein R^1 is selected
from t-butyl, anthracenyl or phenanthracenyl.

47.   The compound of Claim 40 wherein R^5 is 2,6-
di(C_1-C_5 alkyl)phenyl group.

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48.   The compound of Claim 46 wherein R^5 is 2,6-
di(isopropyl)phenyl.

49.   The compound of Claim 40 wherein X is selected
15   from nitro, sulfonate or perfluoromethyl.

50.   The compound of Claim 40 wherein R^1 is selected
from a hydrocarbyl terminated oxyhydrocarbylene group
represented by the formula -(BO)$_z$$R^7$ wherein B is
20   independently selected from a C_1-C_4 alkylene or arylene, O
is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-4.

51.   The compound of Claim 40 wherein R^5 is selected
from an aryl group substituted with a hydrocarbyl
25   terminated oxyhydrocarbylene group represented by the
formula -(BO)$_z$$R^7$ wherein B is independently selected from
a C_1-C_4 alkylene or an arylene, O is oxygen, R^7 is a C_1-C_{11}
hydrocarbyl and z is 1-4.

30   52.   The compound of Claim 40 wherein R^5 is selected
from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is
phenanthracenyl.

53.   The compound of Claim 40 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenyl.

54.   The compound of Claim 51, 52 or 53 wherein R^1 and R^5 together represent a polyoxyhydrocarbylene group.

55.   The compound of Claim 51, 52 or 53 wherein R^5 is a 2,6-di(C_1-C_4 alkyl)-4-nitrophenyl group.

56.   The compound of Claim 54 wherein X is selected from nitro group.

57.   The compound of Claim 50 wherein X is selected from nitro group, perfluoroalkyl group, sulfonate group, or halo atom.

58.   The compound of Claim 50 wherein R^1 and R^5 together represent an oxyalkylene group.

59.   The compound of Claim 40 wherein
    R^1 is anthracenyl;
    R^2, R^3 and R^4 are each hydrogen;
    R^5 is 2,6-di(isopropyl) phenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium;
    A is oxygen; and
    X is hydrogen.

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60. The compound of Claim 40 wherein
     R^1 is phenanthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is hydrogen.

61. The compound of Claim 40 wherein
     R^1 is phenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is hydrogen.

62. The compound of Claim 40 wherein
     R^1 is anthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is hydrogen.

63. The compound of Claim 40 wherein

R^1 is 10-nitroanthracenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl) phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

64. The compound of Claim 40 wherein

R^1 is phenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl) phenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

65. The compound of Claim 40 wherein

R^1 is 10-nitroanthracenyl;

R^2, R^3 and R^4 are each hydrogen;

R^5 is 2,6-di(isopropyl)-4-nitrophenyl;

R^6 is phenyl;

L is triphenyl phosphine;

M is selected from nickel or palladium;

A is oxygen; and

X is nitro.

66. The compound of Claim 40 wherein
     R^1 is phenanthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is nitro.

67. The compound of Claim 40 wherein
     R^1 is 10-nitroanthracenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is hydrogen.

68. The compound of Claim 40 wherein
     R^1 is terphenyl;
     R^2, R^3 and R^4 are each hydrogen;
     R^5 is 2,6-di(isopropyl) phenyl;
     R^6 is phenyl;
     L is triphenyl phosphine;
     M is selected from nickel or palladium;
     A is oxygen; and
     X is hydrogen.

69.   The compound of Claim 40 wherein
      R^1 is terphenyl;
      R^2, R^3 and R^4 are each hydrogen;
      R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
      R^6 is phenyl;
      L is triphenyl phosphine;
      M is selected from nickel or palladium;
      A is oxygen; and
      X is hydrogen.

70.   The compound of Claim 40 wherein
      R^1 is terphenyl;
      R^2, R^3 and R^4 are each hydrogen;
      R^5 is 2,6-di(isopropyl) phenyl;
      R^6 is phenyl;
      L is triphenyl phosphine;
      M is selected from nickel or palladium;
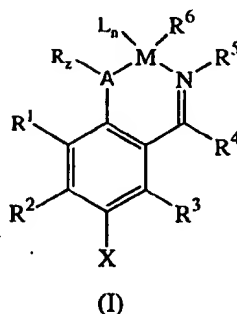   A is oxygen; and
      X is nitro.

71.   The compound of Claim 40 wherein
      R^1 is terphenyl;
      R^2, R^3 and R^4 are each hydrogen;
      R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
      R^6 is phenyl;
      L is triphenyl phosphine;
      M is selected from nickel or palladium;
      A is oxygen; and
      X is nitro.

72. The compound of Claim 40 wherein
    R^1 is 10-nitroanthracenyl;
    R^2, R^3 and R^4 are each hydrogen;
    R^5 is 2,6-di(isopropyl) phenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium;
    A is oxygen; and
    X is nitro.

73. The compound of Claim 40 wherein
    R^1 is phenyl;
    R^2, R^3 and R^4 are each hydrogen;
    R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium;
    A is oxygen; and
    X is hydrogen.

74. The compound of Claim 40 wherein
    R^1 is phenyl;
    R^2, R^3 and R^4 are each hydrogen;
    R^5 is 2,6-di(isopropyl)-4-nitrophenyl;
    R^6 is phenyl;
    L is triphenyl phosphine;
    M is selected from nickel or palladium;
    A is oxygen; and
    X is nitro.

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75.   A process for forming a polyolefin comprising
contacting at least one olefinic compound with a catalyst
composition comprising a compound represented by the
general formula:

(I)

wherein

R independently represents hydrogen atom; C_1-C_{11}
alkyl; aryl; or substituted aryl, provided that R
represents at least one hydrogen atom, and z is 1 when A
is oxygen or sulfur or z is 2 when A is nitrogen.

R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl;
substituted aryl wherein the substitution group is
selected from C_1-C_4 alkyl, perfluoroalkyl, nitro,
sulfonate or halo group; arylalkyl; siloxyl (-OSiA$_3$ where.
A is selected from phenyl or C_1-C_4 alkyl); nitro group;
sulfonate group; halo atom; or a hydrocarbyl terminated
oxyhydrocarbylene group (-(BO)$_z$$R^7$ wherein each B
independently is selected from a C_1-C_4 alkylene or an
arylene group, O represents oxygen, R^7 represents a C_1-C_{11}
hydrocarbyl group and z is an integer of 1 to 4);

R^2 represents hydrogen atom, aryl, substituted aryl,
C_1-C_{11} alkyl, halogen atom or R^1 and R^2, together, provide a
hydrocarbylene or substituted hydrocarbylene which forms
an aromatic or non-aromatic carbocyclic ring;

R^3 represents hydrogen;

R^4 represents hydrogen atom, a C_1-C_{11} alkyl; an aryl; substituted aryl group; or R^3 or R^4, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R^5 represents a C_1-C_{11} alkyl; cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C_1-C_4 alkyl, the para position (with respect to the N-R^5 bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C_1-C_4 alkyl, sulfonate or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group ($-(BO)_2R^7$); or R^1 and R^5 together form an oxyhydrocarbylene chain, $-(BO)_mB-$, wherein each B is independently selected from a C_1-C_4 alkylene group or an arylene group and m is an integer of 1-4;

n represents an integer of 0 or 1;

R^6 represents, when n is 1, an unsubstituted or substituted aromatic group; a C_1-C_{11} alkyl; a hydrogen atom or halogen atom or when, n is 0, R^6 represents an allyl group or substituted allyl group;

L represents a coordination ligand selected from triphenylphosphine, tri(C_1-C_6 alkyl) phosphine, tricycloalkyl phosphine, diphenyl alkyl phosphine, dialkyl phenylphosphine, triphenoxyphosphine, trialkylamine, C_2-C_{20} alkene, substituted C_2-C_4 alkene, C_1-C_4 alkoxy, pyridine, di(C_1-C_3 alkyl) ether, tetrahydrofuran, or a nitrile;

X represents a hydrogen atom or an electron withdrawing group selected from NO_2, halo, sulfonate (SO_3^-), sulfonyl ester (SO_2R), carboxyl (COO^-), a perfluoroalkyl, or a carboxylic ester group;

M represents a Group IV or VIII transition metal selected from Ti, Zr, Hf in the +4 oxidation state or Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt in the +2 oxidation state; and

A represents oxygen, nitrogen or sulfur.

76. The process of Claim 75 wherein the catalyst composition further comprises a phosphine sponge or a Lewis base or mixtures thereof.

77. The process of Claim 75 wherein R^6 represents halogen atom and the composition further comprises a catalyst adjunct selected from a partially hydrolyzed aluminum alkyl compound or an aluminum alkyl compound.

78. The process of Claim 76 wherein the catalyst composition further comprises an adjunct selected from methyl alumoxane or trialkylaluminum, or mixtures thereof.

79. The process of Claim 75 wherein R^1 is selected from aryl group, substituted aryl group or C_3-C_6 alkyl group.

80. The process of Claim 76 or 91 wherein R^1 is selected from aryl group, substituted aryl group or C_3-C_6 alkyl group.

81. The process of Claim 78 wherein R^5 is selected from an aryl group having one or both ortho positions substituted with a C_1-C_4 alkyl group.

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82. The process of Claim 79 wherein R^5 is selected from an aryl group having one or both ortho positions substituted with a C$_1$-C$_4$ alkyl group.

83. The process of Claim 78 wherein R^5 is selected from alkyl or cycloalkyl.

84. The process of Claim 79 wherein R^5 is selected from alkyl or cycloalkyl.

85. The process of Claim 91 wherein X is selected from nitro group, perfluoroalkyl group, sulfonate group or halo atom.

86. The process of Claim 75 wherein X is selected from nitro group, perfluoroalkyl group, sulfonate group or halo atom.

87. The process of Claim 75, 76, 77, 78 or 79 wherein M is nickel or palladium atom.

88. The process of Claim 75, 76, 77, 78 or 79 wherein the olefinic compound is selected from a C$_2$-C$_3$ olefinic compound alone.

89. The process of Claim 88 wherein the olefinic compound is ethylene.

90. The process of Claim 88 wherein the olefinic compound further comprises at least one functionalized alpha-olefin.

91. The process of Claim 90 wherein the
functionalized alpha-olefin is selected from carboxylic
acid of the formula $CH_2=CH(CH_2)_mCOOH$, carboxylic acid ester
of the formula $CH_2=CH(CH_2)_mCO_2R^7$ or $CH_2=CHOCOR^7$, an alkyl
vinyl ether of the formula $CH_2=CH(CH_2)_mOR^7$, vinyl ketones
of the formula $CH_2=CH(CH_2)_mC(O)R^7$, vinyl alcohol of the
formula $CH_2=CH(CH_2)_mOH$, wherein m is an integer of 0 to 10
and R^7 is a C_1-C_{10} hydrocarbyl, aryl or substituted aryl
group; vinylamines of the formula $CH_2=CH(CH_2)_mNR^8_2$, wherein
each R^8 is independently selected from hydrogen atom or
C_1-C_{11} alkyl or aryl; a cycloolefin having a functional
group selected from an ester, carboxylic acid, halogen
atom, or amine group; unsaturated dicarboxylic acid
anhydride; carbon monoxide; vinyl halide; or mixtures
thereof.

92. The process of Claim 75 wherein the catalyst
composition further comprises a Lewis base selected from
ethers, esters, aldehydes, ketones, alcohols, amides,
organocarbonates and organonitro compounds and mixtures
thereof.

93. The process of Claim 75 wherein the catalyst is
used in the presence of water and the molar ratio of
water to catalyst is from 0 to 10^2.

94. The process of Claim 92 wherein the Lewis base
is an ether selected from a di(C_1-C_{18} alkyl) ether, aryl
ethers, aryl alkyl ethers, cyclic ethers, polyethers, or
mixtures thereof.

95. The process of Claim 75 wherein the
polymerization is carried out in solution and the
polymerization solvent comprises an ether or polyether.

100. The process of Claim 92 wherein the Lewis base
is an amide represented by the formula:

$$\underset{R^{12}-\overset{\displaystyle\overset{O}{\parallel}}{C}-N\ R^{13}\ R^{14}}{}$$

wherein R^{12} and R^{13} each independently represents a C_1-C_{11}
hydrocarbyl and R^{14} represents hydrogen or a C_1-C_{11}
hydrocarbyl group.

101. The process of Claim 92 wherein the Lewis base
is an organonitro compound selected from C_1-C_{11}
nitroalkanes, C_1-C_{11} polynitro alkanes, and
mononitroaromatics.

102. The process of Claim 92, 94, 97, 98, 99, 100 or
101 wherein the Lewis base is present in a molar ratio of
Lewis base to catalyst compound I from about 10^0 to about
10^4.

103. The process of Claim 75 wherein R^1 is selected
from a hydrocarbyl terminated oxyhydrocarbylene group
represented by the formula $-(BO)_z R^7$ wherein each B is
independently selected from a C_1-C_4 alkylene or an arylene
group, O is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-
4.

104. The process of Claim 75 wherein R^5 is selected
from an aryl group substituted with a hydrocarbyl
terminated oxyalkylene group represented by the formula
$-(BO)_z R^7$ wherein B is a C_1-C_4 alkylene, O is oxygen, R^7 is a
C_1-C_{11} hydrocarbyl and z is 1-4.

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105. The process of Claim 75 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is anthracenyl.

106. The process of Claim 75 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenanthracenyl.

107. The process of Claim 75 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenyl.

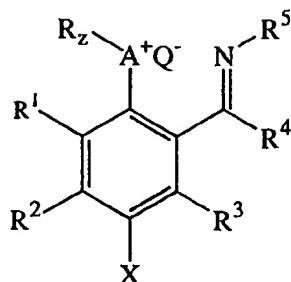108. The process of Claim 75 wherein R^1 and R^5 together represent an oxyhydrocarbylene group.

109. The process of Claim 76, 77, 78, 79, 81, 82, 83, 84, 85 or 86 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

110. The process of Claim 103 or 104 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

111. A process for forming a polyolefin comprising contacting at least one olefinic compound with a catalyst composition comprising:
    (i) a compound represented by the formula:

$$\underset{R^1}{\overset{R_z{-}A^+Q^-}{\bigcirc}}\overset{N{-}R^5}{\underset{R^4}{}}$$

(V)

wherein

R independently represents hydrogen atom, C_1-C_{11} alkyl; aryl; or substituted aryl, provided that R represents at least one hydrogen atom, and z is 1 when A is oxygen or sulfur or z is 2 when A is nitrogen;

R^1 represents a hydrogen atom; C_1-C_{11} alkyl; aryl; substituted aryl wherein the substitution group is selected from C_1-C_4 alkyl, perfluoroalkyl, nitro, sulfonate or halo group; arylalkyl; or siloxyl (-OSiA_3 where A is selected from phenyl or C_1-C_4 alkyl); nitro group; sulfonate group; halo atom; or a hydrocarbyl terminated oxyhydrocarbylene group, -(BO)$_z$R^7, wherein each B independently is selected from a C_1-C_4 alkylene or an arylene group, O represents oxygen, R^7 represents a C_1-C_{11} hydrocarbyl group and z is an integer of 1 to 4;

R^2 represents hydrogen atom, aryl, substituted aryl, C_1-C_{11} alkyl, halogen atom or R^1 and R^2, together, provide a hydrocarbylene or substituted hydrocarbylene which forms an aromatic or non-aromatic carbocyclic ring;

R^3 represents hydrogen;

R^4 represents hydrogen atom, a C_1-C_{11} alkyl; an aryl; substituted aryl group; or R^3 or R^4, together, provide a hydrocarbylene or substituted hydrocarbylene forming a non-aromatic carbocyclic ring;

R^5 represents a C_1-C_{11} alkyl; cycloalkyl; aryl group; a substituted aryl having one or both ortho positions of the aromatic group substituted with a C_1-C_4 alkyl, the para position (with respect to the N-R^5 bond) substituted with a hydrogen, nitro, trifluoromethyl, halogen, methoxy, C_1-C_4 alkyl, sulfonate or fused or unfused aryl group; or a hydrocarbyl terminated oxyhydrocarbylene group (-$(BO)_zR^7$); or R^1 and R^5 together form an oxyhydrocarbylene chain, -$(BO)_mB$-, wherein each B is independently selected from a C_1-C_4 alkylene group or an arylene group and m is an integer of 1-4;

X represents any electron withdrawing group selected from NO_2, halo, sulfonate (SO_3^-), sulfonyl ester (SO_2R), carboxyl (COO^-), a perfluoroalkyl, a carboxylic ester or a hydrogen atom;

A represents oxygen, nitrogen or sulfur;

Q represents alkali metal cation selected from sodium, potassium or lithium; and

(ii) a transition metal organic complex, wherein said transition metal has a valence state of +2 or +4 and is selected from a Group IV or VIII transition metal of Ti, Zr, Hf, Co, Ni, Ru, Rh, Pd, Os, Ir or Pt.

112. The process of Claim 111 wherein the transition metal organic complex is a complex of formula $R^6(L)_2MY$ wherein

R^6 represents an unsubstituted or substituted aromatic group; a C_1-C_{11} alkyl; an allyl or substituted allyl group;

L represents a coordination ligand selected from
triphenylphosphine, tri(C_1-C_6 alkyl)phosphine,
tricylcoalkyl phosphine, diphenyl alkyl phosphine,
dialkyl phenylphosphine, triphenoxyphosphine,
trialkylamine, pyridine, C_2-C_{20} alkene, substituted C_2-C_4
alkene, C_1-C_4 alkoxy, di(C_1-C_3 alkyl) ether,
tetrahydrofuran, or a nitrile;

Y represents a halogen atom selected from chloro,
bromo or fluoro; and

M represents a transition metal selected from a
Group IV or Group VIII metal of Ti, Zr, Hf, Co, Ni, Ru,
Rh, Pd, Os, Ir or Pt.

113. The process of Claim 112 wherein the complex is
bis-triphenylphosphine nickel(phenyl) chloride.

114. The process of Claim 112 wherein the catalyst
composition further comprises a phosphine sponge.

115. The process of Claim 112 wherein R^6 represents
halogen atom and the composition further comprises a
catalyst adjunct selected from a partially hydrolyzed
aluminum alkyl compound or an aluminum alkyl or mixtures
thereof.

116. The process of Claim 115 wherein the catalyst
composition further comprises an adjunct selected from
methyl alumoxane or trialkylaluminum or mixtures thereof.

117. The process of Claim 112 wherein R^1 is selected
from an aryl group, substituted aryl group or C_3-C_6 alkyl
group.

118. The process of Claim 114 or 115 wherein R^1 is selected from an aryl group, substituted aryl group or C_3-C_6 alkyl group.

119. The process of Claim 117 wherein R^5 is selected from an aryl group having one or both ortho positions substituted with a C_1-C_4 alkyl group.

120. The process of Claim 118 wherein R^5 is selected from an aryl group having one or both ortho positions substituted with a C_1-C_4 alkyl group.

121. The process of Claim 117 wherein R^5 is selected from alkyl or cycloalkyl.

122. The process of Claim 118 wherein R^5 is selected from alkyl or cycloalkyl.

123. The process of Claim 114 wherein X is selected from a nitro group, perfluoroalkyl group, sulfonate group or halogen atom.

124. The process of Claim 115 wherein X is selected from a nitro group, perfluoroalkyl group, sulfonate group or halogen atom.

125. The process of Claim 112, 114, 115, 116 or 117 wherein the transition metal of said complex is selected from nickel or palladium atom.

126. The process of Claim 112, 114, 115, 116 or 117 wherein the olefinic compound is a C_2-C_3 olefinic compound.

127. The process of Claim 126 wherein the olefinic compound is ethylene.

128. The process of Claim 126 wherein the olefinic compound further comprises at least one functionalized olefin.

129. The process of Claim 128 wherein the functionalized olefin is selected from a carboxylic acid of the formula $CH_2=CH(CH_2)_mCOOH$, carboxylic acid ester of the formula $CH_2=CH(CH_2)_mCO_2R^7$ or $CH_2=CHOCOR^7$, an alkyl vinyl ether of the formula $CH_2=CH(CH_2)_mOR^7$, vinyl ketones of the formula $CH_2=CH(CH_2)_mC(O)R^7$, vinyl alcohol of the formula $CH_2=CH(CH_2)_mOH$, wherein m is an integer of 0 to 10 and R^7 is a C_1-C_{10} hydrocarbyl, aryl or substituted aryl group; vinylamines of the formula $CH_2=CH(CH_2)_mNR^8_2$ wherein each R^8 is independently selected from hydrogen atom or C_1-C_{11} alkyl or aryl; a cycloolefin having a functional group selected from an ester, carboxylic acid, halogen atom, hydroxyl group, or amine group; unsaturated dicarboxylic acid anhydride; carbon monoxide; vinyl halide; or mixtures thereof.

130. The process of Claim 128 wherein the functionalized olefin is a hydroxyl substituted or ester substituted norbornene.

131. The process of Claim 111 wherein the catalyst composition further comprises a phosphine sponge or a Lewis base or mixtures thereof.
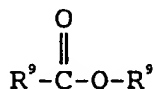
132. The process of Claim 111 wherein the catalyst
composition further comprises a Lewis base selected from
ethers, esters, aldehydes, ketones, alcohols, amides,
organocarbonates and organonitro compounds and mixtures
thereof.

133. The process of Claim 111 wherein the catalyst
is used in the presence of water and the molar ratio of
water to catalyst is from 0 to about 10^2.

134. The process of Claim 132 wherein the Lewis base
is an ether selected from di(C_1-C_{18} alkyl)ethers, aryl
ethers, aryl alkyl ethers, cyclic ethers, polyethers, or
mixtures thereof.

135. The process of Claim 134 wherein the
polymerization is carried out in solution and the
polymerization solvent comprises an ether or polyether.

136. The process of Claim 132 wherein the Lewis base
is an organic ester represented by the formula:

$$R^9-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-R^9$$

wherein each R^9 independently represents a C_1-C_{11} alkyl
group.

137. The process of Claim 132 wherein the Lewis base
is an aldehyde or ketone represented by the formula:

$$\begin{array}{c} O \\ \parallel \\ R^{10}\text{-}C\text{-}R^{11} \end{array}$$

wherein R^{10} represents an unsubstituted or substituted C_1-
C_{12} hydrocarbyl group and R^{11} represents a hydrogen atom or
a R^{10} group.

138. The process of Claim 132 wherein the Lewis base
is a monohydric or polyhydric alcohol, said alcohol
having a hydrocarbyl group composed of a C_1-C_{12} alkyl,
aryl, alkaryl or aralkyl group.

139. The process of Claim 132 wherein the Lewis base
is an amide represented by the formula:

$$\begin{array}{c} O \\ \parallel \\ R^{12}\text{-}C\text{-}N \;\; R^{13} \;\; R^{14} \end{array}$$

wherein R^{12} and R^{13} each independently represents a C_1-C_{11}
hydrocarbyl and R^{14} represents hydrogen or a C_1-C_{11}
hydrocarbyl and R^{14} represents hydrogen or a C_1-C_{11}
hydrocarbyl group.

140. The process of Claim 132 wherein the Lewis base
is an organonitro compound selected from C_1-C_{11}
nitroalkanes, C_1-C_{11} polynitro alkanes, and mono-
nitroaromatics.

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141. The process of Claim 132, 134, 136, 137, 138, 139 or 140 wherein the Lewis base is present in a molar ratio of Lewis base to compound V from about 10^0 to about 10^4.

142. The process of Claim 111 wherein R^1 is selected from a hydrocarbyl terminated oxyhydrocarbylene group represented by the formula $-(BO)_z R^7$ wherein each B is independently selected from a C_1-C_4 alkylene or an arylene, O is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-4.

143 The process of Claim 111 wherein R^5 is selected from an aryl group substituted with a hydrocarbyl terminated oxyalkylene group represented by the formula $-(BO)_z R^7$ wherein B is a C_1-C_4 alkylene, O is oxygen, R^7 is a C_1-C_{11} hydrocarbyl and z is 1-4.

144. The process of Claim 111 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is anthracenyl.

145. The process of Claim 111 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenanthracenyl.

146. The process of Claim 111 wherein R^5 is selected from a 2,6-di(C_1-C_4 alkyl) phenyl and R^1 is phenyl.

147. The process of Claim 111 wherein R^1 and R^5 together represent a polyoxyhydrocarbylene group.

148. The process of Claim 112, 113, 114, 115, 116, 117, 119, 120, 121, 122, 123 or 124 wherein the catalyst composition further comprises a Lewis base selected from ethers, esters, aldehydes, ketones, alcohols, amides, organocarbonates, organonitro compounds and mixtures thereof.

149. The process of Claim 111 wherein the transition metal organic complex is a complex of a C_5-C_{10} cycloalkyldiene, or a trihydrocarbyl phosphine wherein each hydrocarbyl group is independently selected from C_1-C_{10} alkyl, phenyl or cycloalkyl group.

150. The process of Claim 112 wherein the complex is a nickel bis-cyclooctadiene.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.

US CL :502/155, 167; 525/245, 248; 526/170, 171; 548/402, 453

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/155, 167; 525/245, 248; 526/170, 171; 548/402, 453

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,557,023 A (SOMOGYVARI et al) 17 September 1996 (17-09-96).	1-150
A	US 4,537,982 A (STARZEWSKI et al) 27 August 1985 (27-08-85).	1-150
A	US 4,382,153 A (BEACH et al) 03 May 1983 (03-05-83).	1-150
A	US 3,686,159 A (BAUER et al) 22 August 1972 (22-08-72).	1-150

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 JUNE 1998	**23 JUN 1998**

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer BERNARD LIPMAN
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C07D 207/00, 209/00, 487/02, 491/02, 495/02, 497/02; B01J 31/00; C08F 4/00